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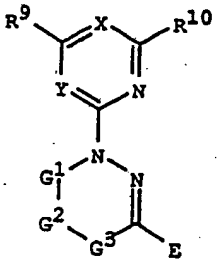
(54) Title: FUNGICIDAL 1,3,4-OXADIAZINES AND 1,3,4-THIADIAZINES



(I)

I

(57) Abstract

Fungicidal 1,3,4-oxadiazines and 1,3,4-thiadiazines of general formula (I) are disclosed, wherein G^1 is $-CR^1R^7-$, $-(CHR^1CHR^2)-$, $-(CHR^1CHR^2CHR^3)-$, or $-(CHR^1CHR^2CHR^3CHR^4)-$; G^2 is -O-, -S-, -S(O)-, $-S(O)_2-$, or $-NR^{27}-$; G^3 is $-CR^4R^8-$, $-(CHR^5CHR^6)-$, or $-(CHR^3CHR^5CHR^6)-$ or a direct bond; X is N or CR^{13}; Y is N or CR^{13}; and E, R^9, and R^{10} are various groups.

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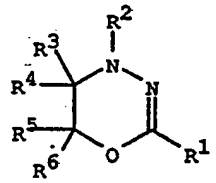
TITLE

FUNGICIDAL 1,3,4-OXADIAZINES AND 1,3,4-THIADIAZINES

This invention relates to heterocyclic thiadiazines and related heterocycles useful as agricultural fungicides and compositions containing them.

BACKGROUND OF THE INVENTION

U.S.S.R. patent 461,929 generically discloses oxadiazines of Formula i and ii



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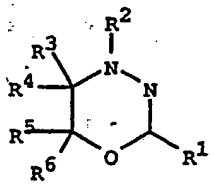


ii

wherein:

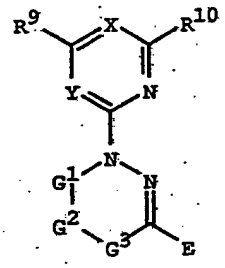
R^1, R^3, R^4, R^5, and R^6 are hydrogen, alkyls, carboxyalkyls, aminoalkyls, phenyl, substituted phenyls, pyridyls, quinolyls, furyls, or thienyls, and

R^2 is alkyl, substituted alkyl, phenyl, substituted phenyl, or heteroaryl.

U.S.S.R. 461,929 does not specifically name any of the compounds of the instant invention, nor is any utility for the compounds disclosed, in this patent.

SUMMARY OF THE INVENTION

This invention pertains to compounds of Formulae I, II, III and IV including all geometric and stereo-isomers, agriculturally-suitable salts thereof, agriculturally-suitable metal complexes thereof, compositions containing them and their use as fungicides.



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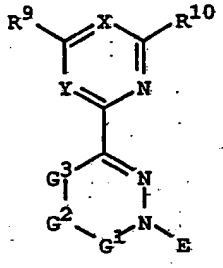

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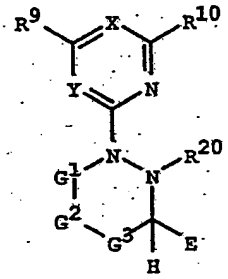
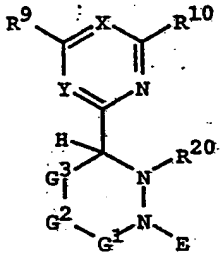


III



IV

wherein:

$-G^1-G^2-G^3-$ taken together with the attached atoms form a 5-8 membered ring, wherein

$-G^1-$ is $-CR^1R^7-$; $-(CHR^1CHR^2)-$; $-(CHR^1CHR^2CHR^3)-$; or $-(CHR^1CHR^2CHR^3CHR^4)-$;

$-G^2-$ is $-O-$; $-S-$; $-S(O)-$; $-S(O)_2-$ or $-NR^{27}-$;

$-G^3-$ is $-CR^4R^8-$; $-(CHR^5CHR^6)-$; $-(CHR^3CHR^5CHR^6)-$ or a direct bond;

For example, $-G^1-G^2-G^3-$ can be $-CHR^1CHR^2-S-CR^4R^8-$, wherein $-G^1-$ is $-(CHR^1CHR^2)-$, $-G^2-$ is $-S-$, and $-G^3-$ is $-CR^4R^8-$. The directionality of the $-G^1-G^2-G^3-$ linkage is defined as $-G^1-G^2-G^3-$ in compounds of Formulae I and III and $-G^3-G^2-G^1-$ in compounds of Formulae II and IV. Therefore, for example, when $-G^1-$ is $-(CHR^1CHR^2)-$ in a compound of Formula I or III, then the carbon of the CHR^2 unit of $-G^1-$ is bonded to $-G^2-$. In a compound

of Formula II or IV, when $-G^1-$ is $-(CHR^1CHR^2)$, the carbon of the CHR^1 unit is bonded to $-G^2-$.

X is N or CR^{13};

Y is N or CR^{14};

E is H; C_1-C_6 alkyl; C_3-C_7 cycloalkyl optionally substituted with 1-2 methyl; C_1-C_6 haloalkyl; C_1-C_6 alkylthio; C_1-C_6 alkoxy; C_1-C_6 haloalkoxy; or phenyl, phenoxy, phenylthio, phenylamino, phenylmethyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, 2-naphthalenyl, thienyl, furanyl or pyridyl each optionally substituted with R^{11}, R^{12} and R^{28};

R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are each independently H; C_1-C_4 alkyl; C_1-C_4 haloalkyl, halogen, CO_2CH_3, $CO_2CH_2CH_3$, cyano or phenyl optionally substituted with R^{25};

provided that

(i) when $-G^1-$ = $-CR^1R^7-$ and $-G^3-$ = $-CR^4R^8-$, then at least one of R^1, R^4, R^7 and R^8 is hydrogen; in other words the maximum number of carbon atoms in $-G^1-G^2-G^3-$ with geminal disubstitution is one;

(ii) the maximum number of optionally substituted phenyl substituents on $-G^1-G^2-G^3-$ is one;

(iii) $-G^3-$ is other than a direct bond in compounds of Formulae III and IV; and

(iv) $-G^2-G^3-$ is other than $-NR^{27}-$ in compounds of Formulae I and II;

R^9, R^{10} and R^{13} are each independently H; halogen; cyano; hydroxy; C_1-C_6 alkyl; C_1-C_4 haloalkyl; C_1-C_4 alkylthio; C_1-C_4 alkylsulfinyl; C_1-C_4 alkylsulfonyl; C_3-C_6 cycloalkyl optionally substituted with 1-2 methyl groups; C_1-C_4 alkoxy; C_1-C_4 haloalkoxy; C_2-C_4 alkoxyalkyl; C_2-C_4 alkenyl; C_2-C_4 haloalkenyl; C_2-C_4

alkenyloxy; C_2-C_4 alkynyl; C_2-C_4 alkynyloxy; $NR^{29}R^{30}$; or phenyl or phenoxy optionally substituted with R^{31}; or

R^9 and R^{13}, or R^{10} and R^{13}, or R^9 and R^{14} can be taken together to form $-(CH_2)_3-$, $-(CH_2)_4-$ or a fused benzene ring optionally substituted with R^{31};

R^{11}, R^{12}, R^{21}, R^{24}, R^{26} and R^{31} are each independently halogen; C_1-C_4 alkyl; C_1-C_4 haloalkyl; C_1-C_4 alkoxy; or C_1-C_4 haloalkoxy;

R^{14} is H; halogen; C_1-C_2 alkyl; or C_1-C_2 alkoxy;

R^{15}, R^{16}, R^{17}, R^{18}, R^{29} and R^{30} are each independently H or C_1-C_2 alkyl; or

R^{15} and R^{16}, or R^{17} and R^{18}, or R^{29} and R^{30} can be taken together along with the nitrogen atom to which they are attached to form a 4-morpholinyl, pyrrolidinyl or piperidinyl ring;

R^{20} and R^{27} are each independently H; C_1-C_4 alkyl; C_1-C_4 haloalkyl; C_2-C_5 alkylcarbonyl; phenylcarbonyl optionally substituted with R^{21}; C_3-C_4 alkenyl; C_3-C_4 alkynyl; phenylmethyl optionally substituted with R^{21} on the phenyl ring; C_1-C_4 alkylsulfinyl; C_1-C_4 alkylsulfonyl; phenylsulfinyl, phenylsulfonyl or phenoxycarbonyl each optionally substituted with R^{21}; C_2-C_4 alkoxycarbonyl; $C(=O)NR^{22}R^{23}$; $C(=S)NHR^{23}$; $P(=S)(C_1$-C_4 alkoxy$)_2$; $P(=O)(C_1$-C_4 alkoxy$)_2$; or $S(=O)_2NR^{22}R^{23}$;

R^{22} is H or C_1-C_3 alkyl;

R^{23} is C_1-C_4 alkyl; or phenyl optionally substituted with R^{24}; or

R^{22} and R^{23} can be taken together along with the nitrogen atom to which they are attached to form a 4-morpholinyl, pyrrolidinyl, piperidinyl or imidazolyl ring;

R^{25} is 1-2 halogen; C_1-C_4 alkyl; C_1-C_4 haloalkyl; C_1-C_4 alkoxy; C_1-C_4 haloalkoxy; nitro; cyano or C_1-C_4 alkylthio;

R^{28} is halogen; cyano; nitro; hydroxy; hydroxycarbonyl; C_1-C_6 alkyl; C_3-C_6 cycloalkyl; C_1-C_6 haloalkyl; C_1-C_4 alkylthio; C_1-C_4 alkylsulfinyl; C_1-C_4 alkylsulfonyl; $(C_1$-C_4 alkyl)3-silyl; C_2-C_5 alkylcarbonyl; C_2-C_4 alkenyl; C_3-C_4 alkenyloxy; C_2-C_4 alkynyl; C_3-C_4 alkynyloxy; C_1-C_4 alkoxy; C_1-C_4 haloalkoxy; C_2-C_4 alkoxyalkyl; C_2-C_5 alkoxycarbonyl; C_2-C_4 alkoxyalkoxy; $NR^{15}R^{16}$; $C(=O)NR^{17}R^{18}$; or phenyl, phenoxy or phenylthio each optionally substituted with R^{26};

provided that

when E is, C_1-C_6 alkylthio, C_1-C_6 alkoxy, C_1-C_6 haloalkoxy, phenoxy, phenylthio or phenylamino, then E may only substitute compounds of Formula I.

In the above recitations, the term "alkyl", used either alone or in compound words such as "alkylthio" or "haloalkyl" denotes straight-chain or branched alkyl; e.g., methyl, ethyl, *n*-propyl, *i*-propyl, or the different butyl, pentyl or hexyl isomers.

"Alkenyl" denotes straight-chain or branched alkenes; e.g., 1-propenyl, 2-propenyl, 3-propenyl and the different butenyl, pentenyl and hexenyl isomers. "Alkenyl" also denotes polyenes such as 1,3-hexadiene and 2,4,6-heptatriene.

"Alkenyloxy" denotes straight-chain or branched alkenyloxy moieties. Examples of alkenyloxy include $H_2C{=}CHCH_2O$, $(CH_3)_2C{=}CHCH_2O$, $(CH_3)CH{=}CHCH_2O$, $(CH_3)CH{=}C(CH_3)CH_2O$ and $CH_2{=}CHCH_2CH_2O$.

"Alkynyl" denotes straight-chain or branched alkynes; e.g., ethynyl, 1-propynyl, 3-propynyl and the different butynyl, pentynyl and hexynyl isomers.

"Alkynyl" can also denote moieties comprised of multiple triple bonds; e.g., 2,7-octadiyne and 2,5,8-decatriyne.

"Alkynyloxy" denotes straight-chain or branched alkynyloxy moieties. Examples include $HC{\equiv}CCH_2O$, $CH_3C{\equiv}CCH_2O$ and $CH_3C{\equiv}CCH_2CH_2O$.

"Alkylthio" denotes branched or straight-chain alkylthio moieties; e.g. methylthio, ethylthio, and the different propylthio, butylthio, pentylthio and hexylthio isomers.

Examples of "alkylsulfonyl" include CH_3SO_2, $CH_3CH_2SO_2$, $CH_3CH_2CH_2SO_2$, $(CH_3)_2CHSO_2$ and the different butylsulfonyl, pentylsulfonyl and hexylsulfonyl isomers.

"Alkylsulfinyl" denotes both enantiomers of an alkylsulfinyl group. For example, CH_3SO, CH_3CH_2SO, $CH_3CH_2CH_2SO$, $(CH_3)_2CHSO$ and the different butylsulfinyl, pentylsulfinyl and hexylsulfinyl isomers.

"Alkoxy" denotes, for example, methoxy, ethoxy, *n*-propyloxy, isopropyloxy and the different butoxy, pentoxy and hexyloxy isomers.

"Cycloalkyl" denotes, for example, cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl.

The term "halogen", either alone or in compound words such as "haloalkyl", denotes fluorine, chlorine, bromine or iodine. Further, when used in compound words such as "haloalkyl", said alkyl may be partially or fully substituted with halogen atoms which may be the same or different. Examples of "haloalkyl" include F_3C, $ClCH_2$, CF_3CH_2 and CF_3CF_2. Examples of "haloalkenyl" include $(Cl)_2C{=}CHCH_2$ and $CF_3CH_2CH{=}CHCH_2$. Examples of "haloalkynyl" include $HC{\equiv}CCHCl$, $CF_3C{\equiv}C$, $CCl_3C{\equiv}C$ and $FCH_2C{\equiv}CCH_2$. Examples of "haloalkoxy" include CF_3O, CCl_3CH_2O, $CF_2HCH_2CH_2O$ and CF_3CH_2O.

The total number of carbon atoms in a substituent group is indicated by the "C_i-C_j" prefix where i and j

are numbers from 1 to 8. For example, C_1-C_3 alkylsulfonyl designates methylsulfonyl through propylsulfonyl; C_2 alkoxyalkoxy designates CH_3OCH_2O; C_3 alkoxyalkoxy designates, for example, $CH_3OCH_2CH_2O$ or $CH_3CH_2OCH_2O$; and C_4 alkoxyalkoxy designates the various isomers of an alkoxy group substituted with a second alkoxy group containing a total of 4 carbon atoms, examples including $CH_3CH_2CH_2OCH_2O$, and $CH_3CH_2OCH_2CH_2O$. Examples of "alkoxyalkyl" include CH_3OCH_2, $CH_3OCH_2CH_2$, $CH_3CH_2OCH_2$, $CH_3CH_2CH_2CH_2OCH_2$ and $CH_3CH_2OCH_2CH_2$. Examples of "alkoxycarbonyl" include $CH_3OC(=O)$, $CH_3CH_2OC(=O)$, $CH_3CH_2CH_2OC(=O)$, $(CH_3)_2CHOC(=O)$ and the different butoxy-, pentoxy- or hexyloxycarbonyl isomers.

Preferred for reasons of greatest fungicidal activity and/or ease of synthesis are

1. Compounds of Formula I wherein:

Y is N;

E is phenyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, thienyl, or pyridyl each optionally substituted with R^{11}, R^{12} and R^{28};

R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are each independently H or methyl;

R^{11} and R^{12} are each independently F, Cl, methyl, trifluoromethyl, methoxy or trifluoromethoxy;

R^{13} is H;

R^9 and R^{10} are each independently halogen; C_1-C_4 alkyl; cyclopropyl; C_1-C_4 haloalkyl; allyl; or C_2-C_3 alkynyl; or

R^9 and R^{13} can be taken together to form a fused benzene ring optionally substituted with R^{31};

R^{28} is halogen; cyano; C_1-C_4 alkyl; C_1-C_4 haloalkyl; allyl; propargyl; C_1-C_4 alkoxy; C_1-C_4 haloalkoxy; or phenyl or

phenoxy each optionally substituted with R^{26};

R^{31} is halogen; C_1-C_4 alkyl or C_1-C_4 haloalkyl;

and agriculturally-suitable metal complexes thereof.

2. Compounds of Formula III wherein:

Y is N

E is phenyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, thienyl, or pyridyl each optionally substituted with R^{11}, R^{12} and R^{28};

R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are each independently H or methyl;

R^9 and R^{10} are each independently halogen; C_1-C_4 alkyl; cyclopropyl; C_1-C_4 haloalkyl; allyl; or C_2-C_3 alkynyl; or

R^9 and R^{13} can be taken together to form a fused benzene ring optionally substituted with R^{31};

R^{11} and R^{12} are each independently F, Cl, methyl, trifluoromethyl, methoxy or trifluoromethoxy;

R^{13} is H;

R^{20} is H;

R^{27} is H; C_1-C_4 alkyl; C_2-C_5 alkoxycarbonyl; C_3-C_4 alkenyl or C_3-C_4 alkynyl;

R^{28} is halogen; cyano; C_1-C_4 alkyl; C_1-C_4 haloalkyl; allyl; propargyl; C_1-C_4 alkoxy; C_1-C_4 haloalkoxy; or phenyl or phenoxy each optionally substituted with R^{26};

R^{31} is halogen; C_1-C_4 alkyl or C_1-C_4 haloalkyl;

and agriculturally-suitable metal complexes thereof.

3. Compounds of Preferred 1 wherein:
G^2 is O; S or NR^{27};
E is phenyl optionally substituted with R^{11}, R^{12} and R^{28}; indanyl or tetrahydronaphthalenyl; and agriculturally-suitable metal complexes thereof.

4. Compounds of Preferred 3 wherein:
G^2 is O; S; NH or N(C_1-C_4 alkyl);
E is phenyl optionally substituted with R^{11}, R^{12} and R^{28}; and agriculturally-suitable metal complexes thereof.

Specifically preferred for greatest fungicidal activity and/or ease of synthesis are:

3-(4,6-dimethyl-2-pyrimidinyl)-3,6-dihydro-5-phenyl-2H-1,3,4-oxadiazine

3-(4,6-dimethyl-2-pyrimidinyl)-5-(4-ethylphenyl)-3,6-dihydro-2H-1,3,4-oxadiazine

2-(2-chlorophenyl)-4-(4,6-dimethyl-2-pyrimidinyl)-5,6-dihydro-4H-1,3,4-thiadiazine

4-(4,6-dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine

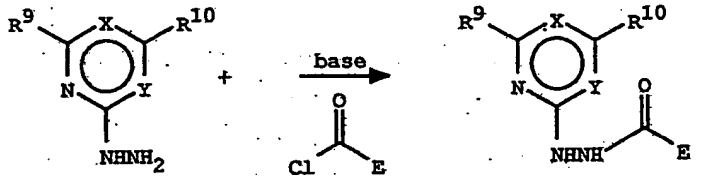
DETAILED DESCRIPTION OF THE INVENTION

Compounds of Formula I wherein E is as described in the Summary of the Invention except that E is not phenoxy, phenylthio, phenylamino, C_1-C_6 alkoxy, C_1-C_6 alkylthio and C_1-C_6 haloalkoxy can be prepared by one or more of the methods described in Equations 1-6 and 13.

Compounds of Formula 2 in Equation 1 can be prepared by reacting hydrazine 1 with an acid chloride and a base such as pyridine or triethylamine at 0°C in a solvent such as dichloromethane, THF, or pyridine (Equation 1). The hydrazines 1 are known in the

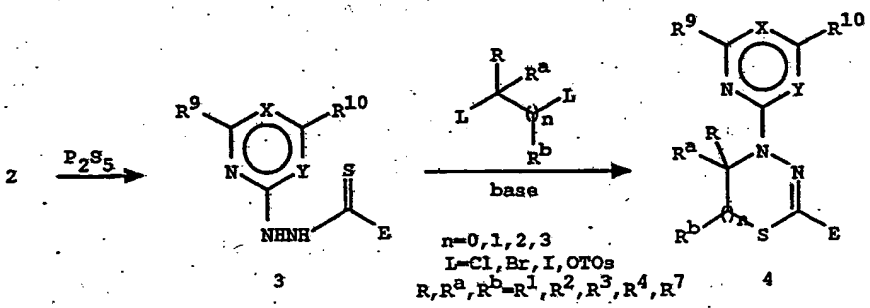
literature (*J. Pest. Sci.*, 1990, 15, 13) and can be prepared by one skilled in the art as taught in EP 293,743-A and by Naito et al. in *Chem. Pharm. Bull.*, 1969, 17, 1467.

Equation 1



Compounds of Formula 4 can be prepared by treatment of hydrazides of Formula 2 with P_2S_5 in pyridine at reflux for 1-2 h to form thiohydrazides of Formula 3, followed by reaction with an appropriate alkylating agent, wherein L can be Cl, Br, I or tosylate, in the presence of two equivalents of base, such as triethylamine (Equation 2). In some cases, additional base such as sodium hydride is necessary to induce cyclization. The cyclization reaction is typically performed at 25° to 100°C in an inert aprotic solvent such as THF or acetonitrile.

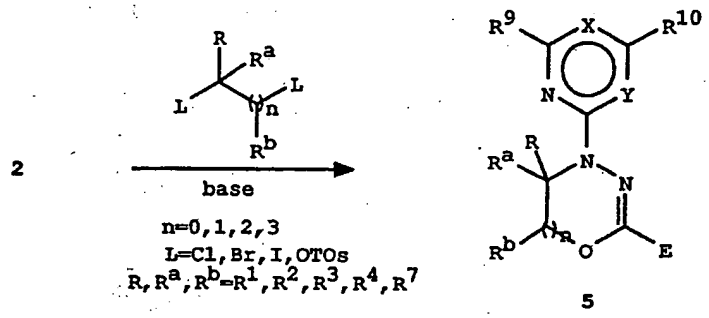
Equation 2



Compounds of Formula 5 can be prepared similarly by treatment of hydrazides of Formula 2 with an alkylating

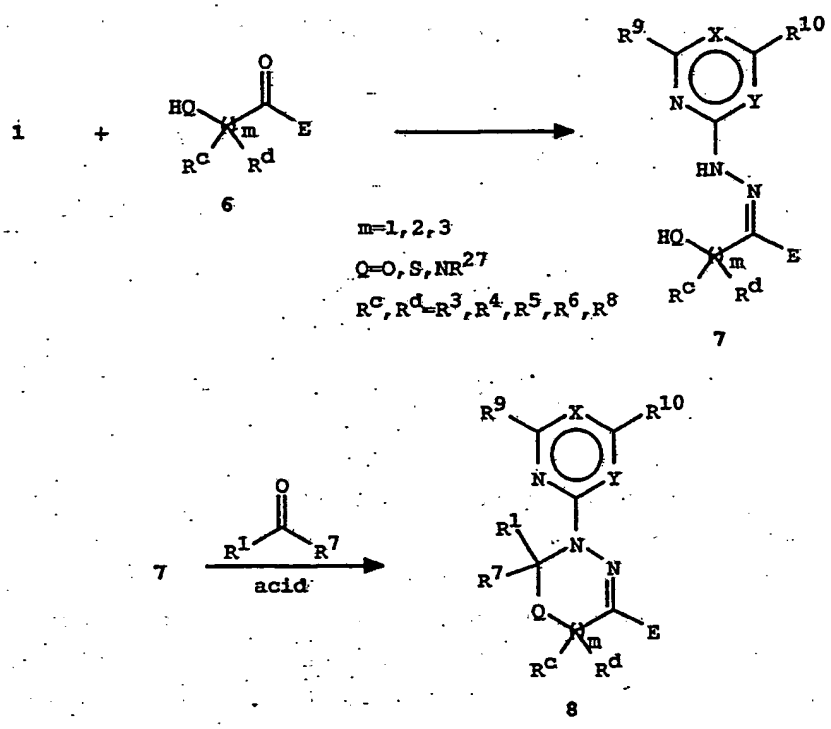
agent and two equivalents of base using the cyclization procedure previously described for the preparation of compounds of Formula 4 (Equation 3).

Equation 3



Compounds of Formula 7 can be prepared by the reaction of hydrazines of Formula 1 with ketones of Formula 6 in a solvent such as acetonitrile, dichloromethane or acetic acid. The desired heterocycles of Formula 8 can be formed by treatment of the resulting product with a ketone or aldehyde in the presence of a catalytic amount of acid such as butanesulfonic acid (Equation 4). This reaction is typically conducted at 25° to 100°C in an anhydrous organic solvent such as THF or acetonitrile for 12 to 24 h.

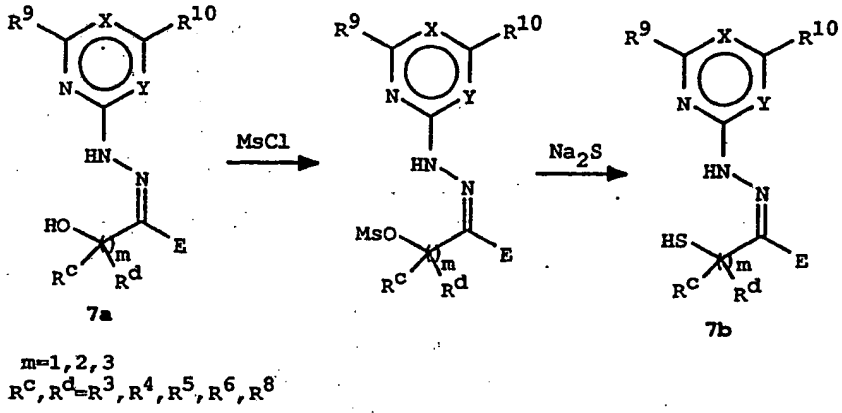
Equation 4



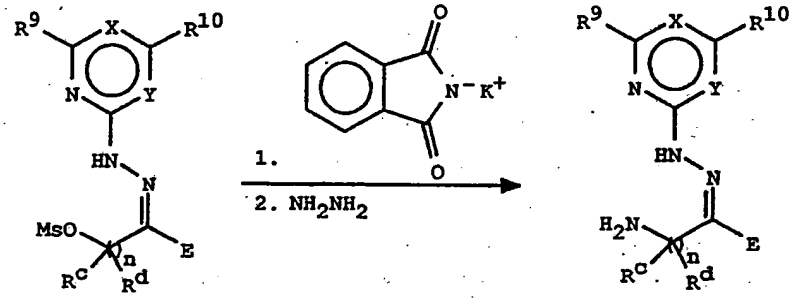
Compounds of Formula **6** wherein m=1 and Q=O can be prepared by α-hydroxylation of a methyl ketone with iodosobenzene as described by Moriarty et al. in *Tetrahedron Lett.*, 1981, 22, 1283.

Thiols of Formula **7b** and amines of Formula **7c** can be prepared as outlined in Equation 5. Alcohols of Formula **7a** (Q=O) can be converted to the corresponding mesylate by methods known in the art. The mesylates can be treated with sodium sulfide to form the thiols **7b**, or they can be reacted with potassium phthalimide and then hydrazine to form amines of Formula **7c**.

Equation 5

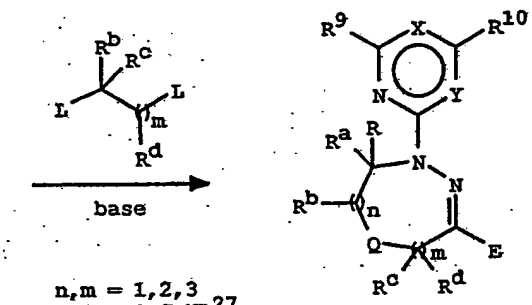


m=1,2,3
$R^c, R^d = R^3, R^4, R^5, R^6, R^8$



Formation of heterocycles of Formula 9 can be accomplished by treatment of hydrazones of Formula 7 with the appropriate alkylating agent as previously described for the preparation of heterocycles of Formula 4 (Equation 6).

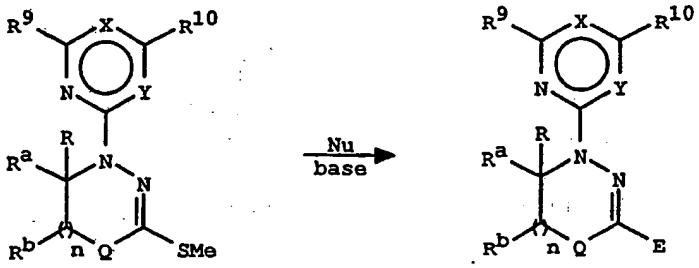
Equation 6



Compounds of Formula I wherein E is phenoxy, phenylthio, phenylamino, C_1-C_6 alkoxy, C_1-C_6 alkylthio or C_1-C_6 haloalkoxy can be prepared by one or more of the methods described in Equations 7-13.

Heterocycles of Formula 11 can be prepared by treating methylthio-substituted compounds of Formula 10 with various nucleophiles in the presence of a base. Suitable nucleophiles can be optionally substituted phenols, thiophenols, or anilines, C_1-C_6 alkylthiols, C_1-C_6 alcohols and C_1-C_6 halo-substituted alcohols (Equation 7).

Equation 7



10 11

Nu = optionally substituted phenol, thiophenol, or aniline; C_1-C_6 alkylthiol; C_1-C_6 alcohol, C_1-C_6 halo-substituted alcohol

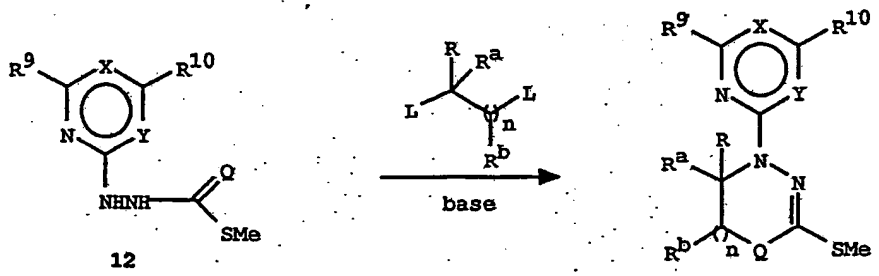
n = 0,1,2,3

Q = O,S,N-R^{27}

R,R^a,R^b = R^1,R^2,R^3,R^4,R^7

The methythio-substituted heterocycles of Formula **10** can be synthesized by reaction of carbazates of Formula **12** with an alkylating agent in the presence of two equivalents of base, such as triethylamine (Equation 8). This type of cyclization was described previously for the preparation of compounds of Formula **4** (Equation 2). Compounds of Formula **12** are known in the literature and can be prepared by one skilled in the art (e.g., see G. W. Stacy, "Heterocyclic Compounds," R. C. Elderfield, ed., Wiley, NY, 1961, vol. 7, p 835).

Equation 8



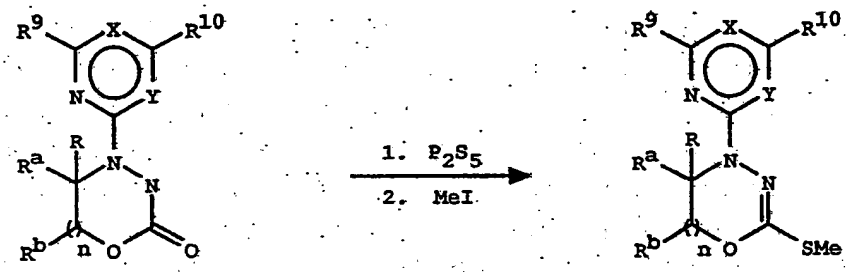
12 10

Q=O,S,NR27

n=0,1,2,3
R,Ra,Rb=R1,R2,R3,R4,R7
L=Cl,Br,I,OTos

Alternatively, compounds of Formula **10a** can be prepared by sequential treatment of carbazates of Formula **13** with P_2S_5 and iodomethane in pyridine (Equation 9). Carbazates of Formula **13** are known in the literature (e.g., see Dox, *J. Am. Chem. Soc.*, 1926, 48, 1951).

Equation 9



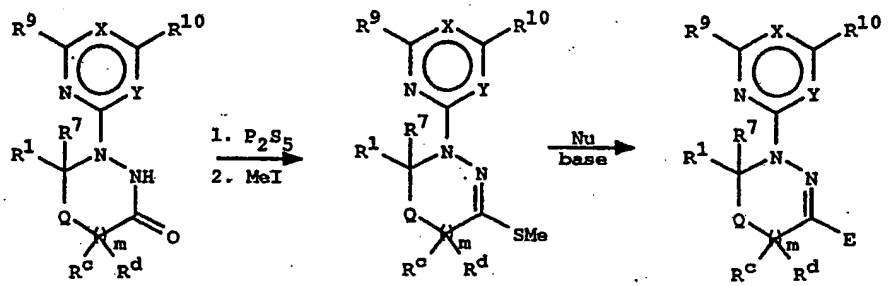
13 10a

n=0,1,2,3
R,Ra,Rb=R1,R2,R3,R4,R7

Methylthio-substituted heterocycles of Formula **15** can be prepared by treating hydrazides of Formula **14** with P_2S_5 in pyridine at reflux and then alkylating the resulting thio derivative with iodomethane in the presence of a base such as triethylamine (Equation 10).

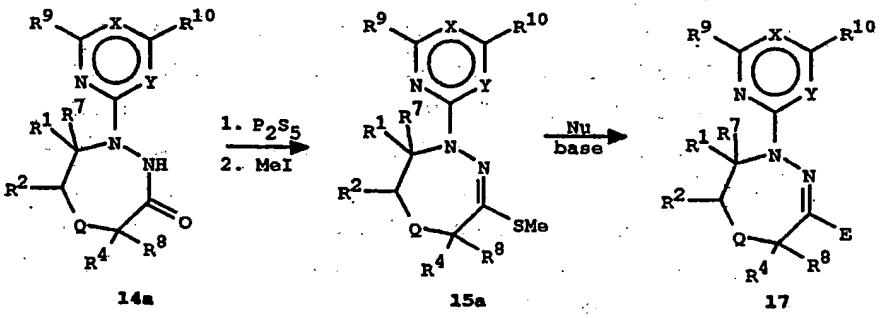
Reaction of compounds of Formula **15** with nucleophiles and base, as previously described for the preparation of compounds of Formula **11** in Equation 7, yields products of Formula **16**. The seven-membered ring analogs, compounds of Formula **17**, can be prepared from hydrazides of Formula **14a** by the same procedure (Equation 10).

Equation 10



14 **15** **16**

m = 1,2,3; Q = O,S,N-R^{27}; R^c,R^d = R^3,R^4,R^5,R^6,R^8



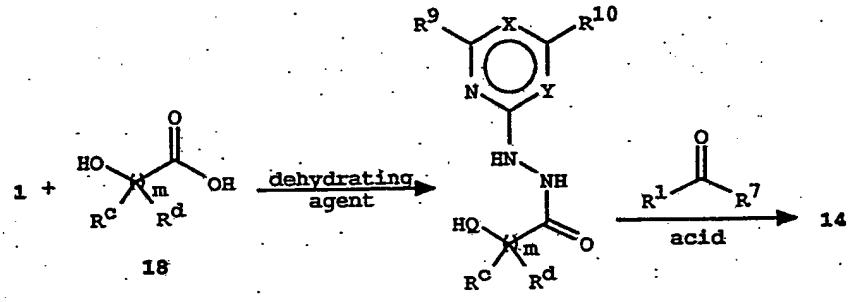
14a **15a** **17**

Q=O,S,NR^{27}

Treatment of hydrazides of Formula **19** with an aldehyde or ketone in the presence of a catalytic amount of acid, such as butanesulfonic acid, yields heterocycles of Formula **14** (Equation 11). The cyclization is typically performed at 25° to 100°C in

an anhydrous organic solvent such as THF or acetonitrile.

Equation 11



m=1,2

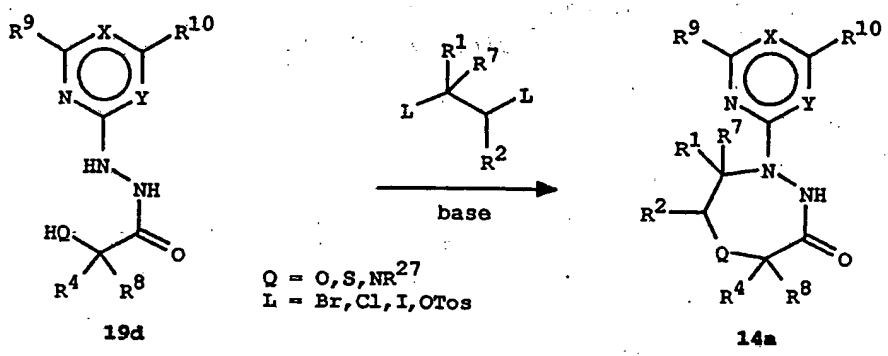
R^c,R^d=R^3,R^4,R^5,R^6,R^8

Q=O,S,NR^{27}

Compounds of Formula **19a** (Q=O) can be synthesized by condensing hydrazine **1** with hydroxyacids of Formula **18** in the presence of a dehydrating agent such as dicyclohexylcarbodiimide in an inert aprotic solvent such as THF or dichloromethane. Hydroxyacids of Formula **18** are well-known to one skilled in the art. Thiols of Formula **19b** (Q=S) and amines of Formula **19c** (Q=NR^{27}) can be prepared by forming the mesylate of alcohols of Formula **19a** followed by displacement with nucleophiles in a manner similar to that previously described for the preparation of compounds of Formulae **7b** and **7c** (Equation 5).

Compounds of **14a** can be prepared by treatment of hydrazides of Formula **19d** (m=1) with the appropriate alkylating agent, as illustrated in Equation 12, according to procedures described above (see Equations 2 and 3).

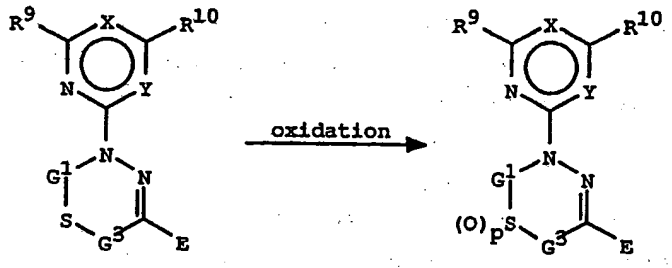
Equation 12



19d 14a

Compounds of Formula **Ib** wherein G^2 is S(O) or $S(O)_2$ can be prepared from the corresponding thio analogue **Ia** by well-known methods for oxidation of sulfur (Equation 13). Typical reagents for this type of oxidation include *m*-chloroperoxybenzoic acid, hydrogen peroxide, sodium metaperiodate, and OXONE® (potassium peroxymonosulfate).

Equation 13



Ia Ib

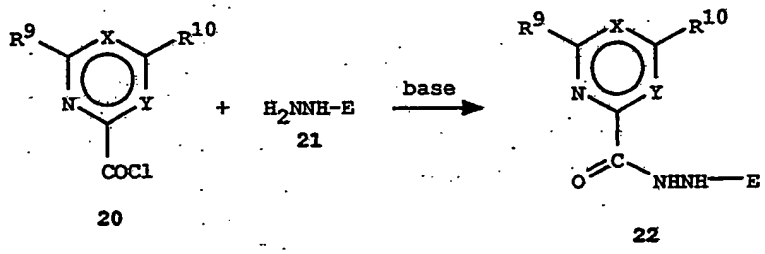
p =1,2

Compounds of Formula **II** can be prepared by one or more of the following methods described in Equations 14-19.

Hydrazides of Formula **22** can be synthesized by the reaction of hydrazine **21** with an acid chloride of

Formula 20 in the presence of a base such as triethylamine or pyridine (Equation 14). Typical solvents for this reaction are dichloromethane and THF.

Equation 14



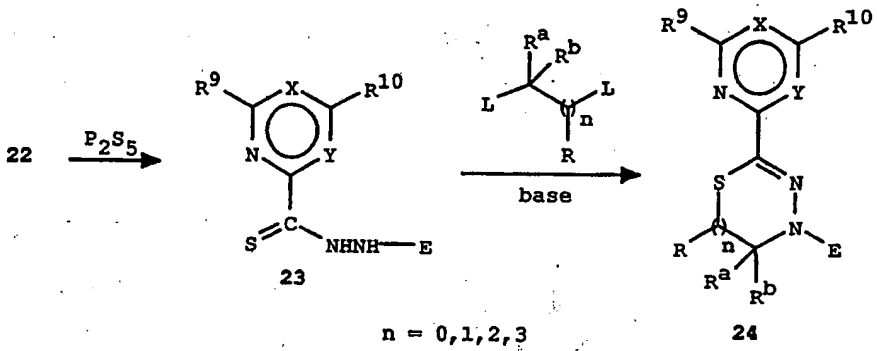
20 22

The acid chloride of Formula 20 can be prepared by treatment of the corresponding carboxylic acid with thionyl chloride. Methods for preparing acid chlorides from carboxylic acids are well-known in the literature.

Procedures for preparing pyrimidine carboxylic acids are described by Sakamoto, T., and Yamanaka, H. in *Heterocycles*, 1981, 15, 583.

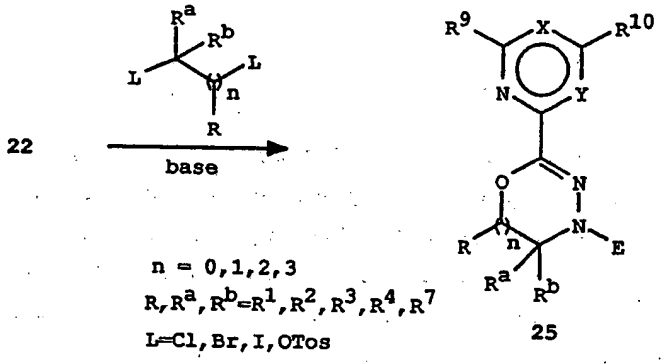
Heterocycles of Formula 24 can be prepared by treating hydrazides of Formula 22 with P_2S_5 in pyridine at reflux to form the thiohydrazides of Formula 23, followed by reaction of 23 with an alkylating agent in the presence of two equivalents of base such as triethylamine (Equation 15). Typically, these reactions are conducted at 25° to 100°C in an inert aprotic solvent such as THF or acetonitrile.

Equation 15



Compounds of Formula **25** can be prepared similarly by treatment of hydrazides of Formula **22** with an alkylating agent and two equivalents of base according to the previously described cyclization procedure (Equation 16).

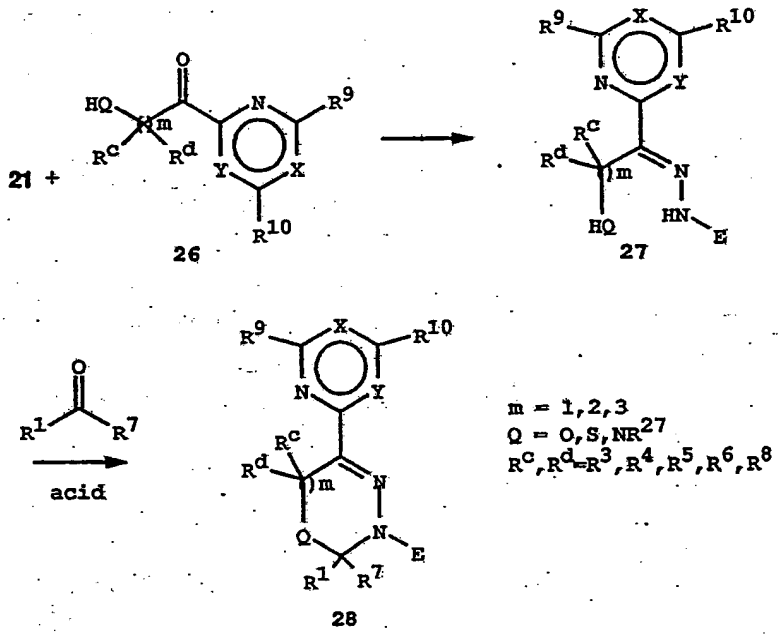
Equation 16



Compounds of Formula **28** can be synthesized by the reaction of hydrazines of Formula **21** with ketones of Formula **26** in a solvent such as dichloromethane or acetonitrile to form hydrazones of Formula **27** (Equation 17). The hydrazone can then be treated with a ketone

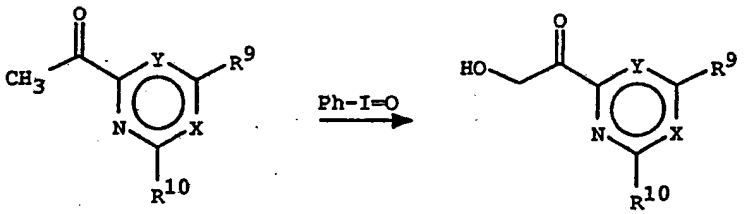
or aldehyde in the presence of a catalytic amount of acid, such as butanesulfonic acid, to form cycloadducts of Formula **28**. This reaction is typically carried out at 25° to 100°C in an anhydrous organic solvent such as THF or acetonitrile.

Equation 17



Hydroxyketones of Formula **26a** (Q=O, m=1) can be prepared by α-hydroxylation of the corresponding methyl ketone **29** with iodosobenzene as described by Moriarty et al. in *Tetrahedron Lett.*, 1981, 22, 1283, and illustrated in Equation 18. Methods to prepare heteroaryl ketones of Formula **29** are well-known in the art. The corresponding thiols of Formula **26b** (Q=S) and amines of Formula **26c** (Q=NR^{27}) can be prepared by methods previously described for thiols and amines of Formulae **7b** and **7c**, respectively (Equation 5).

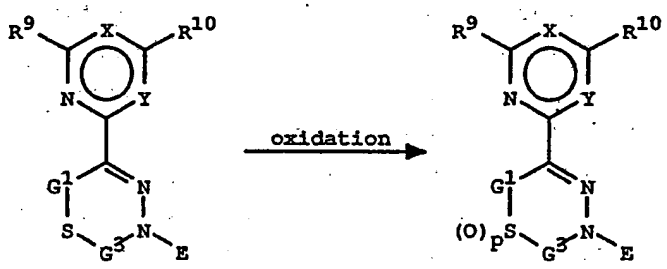
Equation 18



29 26a

Compounds of Formula **IIb** can be synthesized from the corresponding thio analogue of Formula **IIa** by oxidation (Equation 19). Typical reagents for this type of oxidation include *m*-chloroperoxy benzoic acid, hydrogen peroxide, sodium metaperiodate, and OXONE® (potassium peroxymonosulfate).

Equation 19

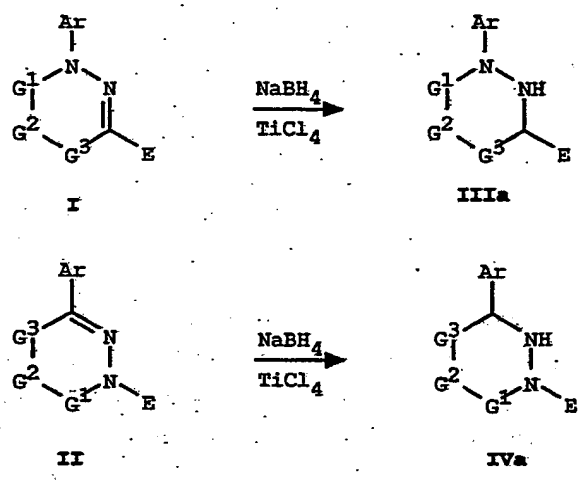


IIa **IIb**

p = 1,2

Compounds of Formulae **IIIa** and **IVa** can be prepared by reduction of compounds of Formulae **I** and **II**, respectively, with sodium borohydride/titanium (IV) chloride according to the procedure taught by Kano et al. in *Synthesis*, 1980, 695, and set forth in Equation 20. In cases where substituents in compounds of Formulae **I** and **II** are not compatible with the reduction conditions, protection and deprotection techniques, which are well-known in the art may be employed.

Equation 20

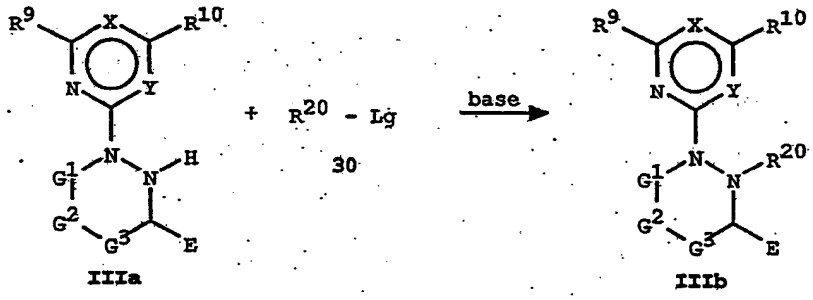


I IIIa

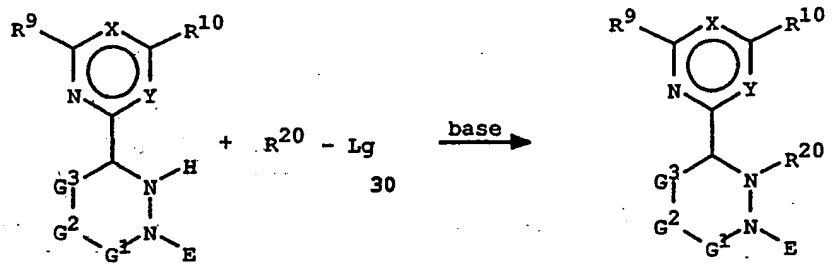
II IVa

Compounds of Formulae **IIIa** and **IVa** can be capped on nitrogen with various substituents (R^{20}) by treating with the appropriate alkylating, acylating, sulfonylating or phosphonylating agent of Formula **30** as shown in Equation 21. The leaving group (Lg) in compounds of Formula **30** may be Cl, Br, I, acetate or other moeity known to act as a leaving group. Typically, these reactions are run in inert solvents such as THF, benzene or dichloromethane in the presence of a tertiary amine base, such as triethylamine, at a temperature ranging from 0° to 100°C.

Equation 21



IIIa 30 IIIb

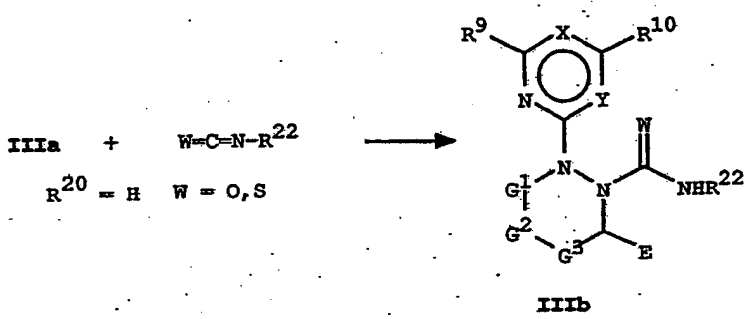


IVa IVb

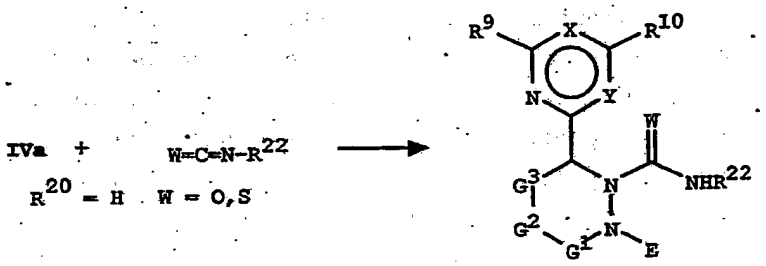
Lg = Cl, Br, I, acetate

Compounds of Formula **IIIb** and **IVb** wherein R^{20} is $C(=O)NR^{22}R^{23}$ or $C(=S)NHR^{23}$ can be prepared by treating compounds of Formulae **IIIa** or **IVa** with an isocyanate or isothiocyanate by methods well-known in the art (Equation 22). Typical solvents for this type of reaction are THF, acetonitrile and dichloromethane.

Equation 22



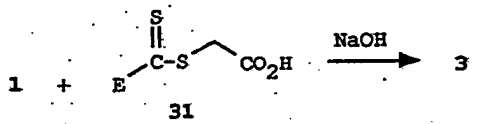
IIIb



IVb

Compounds of Formula 3, as illustrated in Equation 2, can also be prepared by reacting hydrazine 1 with the appropriate carboxymethyl dithioate 31 in aqueous sodium hydroxide at 25°C (Equation 23). Carboxymethyl dithioates are known in the literature and can be prepared by one skilled in the art (see Jensen, K. A. and Pedersen, C., *Acta Chemica Scandinavica*, 1961, 15, 1087).

Equation 23

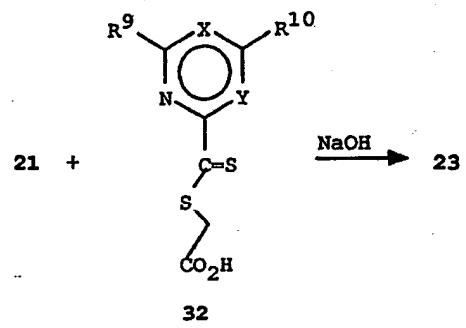


31

Likewise, thiohydrazides of Formula 23, as illustrated in Equation 15, can be synthesized by

reaction of a hydrazine of Formula **21** with a carboxymethyl dithioate of Formula **32** in aqueous sodium hydroxide (Equation 24).

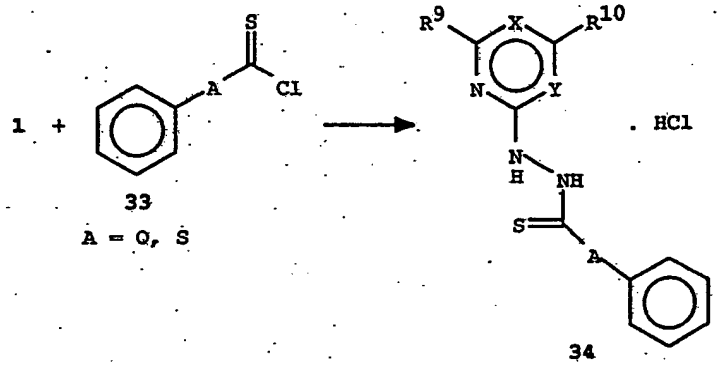
Equation 24

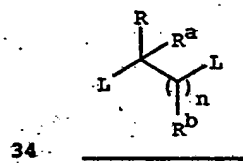


32

Compounds of Formula **11**, wherein E is phenoxy or phenylthio, can also be synthesized by treating a hydrazine of Formula **1** with phenyl-chlorothionoformate or phenyl-chlorodithioformate of Formula **33** to form a thiocarbazate hydrochloride of Formula **34** (Equation 25). This type of reaction is typically run in a solvent such a methylene chloride from about -10°C to 0°C. The cyclization is performed by treating **39** with the appropriate alkylating agent in a solvent mixture of aqueous sodium hydroxide and THF at 25°C.

Equation 25





34 → 11

base

n=0,1,2,3
R,Ra,Rb=R1,R2,R3,R4,R7
L=Cl,Br,I,OTs

The metal complexes of compounds of Formulae I-IV of the instant invention include complexes with copper, zinc, iron, magnesium, or manganese. These complexes can be formed by combining the compound of Formulae I-IV with the metal salt in either aprotic solvents, such as ether or THF, or protic solvents, such as methanol. EP-A-459,662 discloses metal complexes of other nitrogen containing compounds as agricultural fungicides.

EXAMPLE 1

Preparation of 1-(4-ethylphenyl)-2-hydroxyethanone(4,6-dimethyl-2-pyrimidinyl)hydrazone

To a solution of 3.57 g (21.7 mmol) of *p*-ethyl-2-hydroxyacetophenone in 100 mL of acetonitrile was added 3.00 g (21.7 mmol) of 4,6-dimethyl-2-hydrazinopyrimi-

dine, 3Å molecular sieves, and a catalytic amount of butanesulfonic acid. The reaction mixture was stirred overnight at room temperature and then diluted with dichloromethane and chloroform. The organic phase was washed successively with saturated sodium bicarbonate and brine, dried over sodium sulfate, filtered and concentrated. The crude product was passed through a plug of silica gel and triturated with hexanes to yield 3.45 g of product. ^{1}H NMR ($CDCl_3$) δ 10.65 (bs, 1H), 7.61 (d, 2H), 7.15 (d, 2H), 6.47 (s, 1H), 6.10 (bs, 1H), 4.86 (s, 2H), 2.64 (q, 2H), 2.38 (s, 6H), 1.22 (t, 3H).

EXAMPLE 2

Preparation of 3-(4,6-dimethyl-2-pyrimidinyl)-5-(4-ethylphenyl)-3,6-dihydro-2H-1,3,4-oxadiazine

A solution of 1.00 g (3.52 mmol) of 1-(4-ethylphenyl)-2-hydroxyethanone(4,6-dimethyl-2-pyrimidinyl)-hydrazone, 0.21 g (7.04 mmol) of paraformaldehyde, and a catalytic amount of butanesulfonic acid was heated at reflux for 3 h in 20 mL of acetonitrile. After cooling, the reaction mixture was diluted with dichloromethane and chloroform. The organic phase was washed successively with saturated sodium bicarbonate and brine, dried over sodium sulfate, filtered and concentrated. Chromatography on silica gel gave 70 mg of desired product as a gum. ^{1}H NMR ($CDCl_3$) δ 7.66 (d, 2H), 7.21 (d, 2H), 6.56 (s, 1H), 5.54 (s, 2H), 4.81 (s, 2H), 2.67 (q, 2H), 2.42 (s, 6H), 1.24 (t, 3H).

EXAMPLE 3

Preparation of 4-ethylbenzoic acid 2-(4,6-dimethyl-2-pyrimidinyl)hydrazide

4,6-Dimethyl-2-hydrazinopyrimidine (3.72 g, 26.95 mmol) was suspended in 80 mL of pyridine and the reaction mixture was cooled to 10°C. After slowly adding *p*-ethylbenzoyl chloride (5.00 g, 29.66 mmol), the reaction mixture was allowed to warm to room

temperature over 1 h. Addition of ice and water precipitated the product which was filtered and washed with hexanes to yield 6.85 g of a white solid. mp 118-119°C. ^{1}H NMR ($CDCl_3$) δ 9.15 (bs, 1H), 7.8 (d, 2H), 7.35 (bs, 1H), 7.2 (d, 2H), 6.52 (s, 1H), 2.7 (q, 2H), 2.33 (s, 6H), 1.23 (t, 3H).

EXAMPLE 4

Preparation of 4-(4,6-dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine

A solution of 5.30 g (18.52 mmol) of 4-ethylbenzoic acid 2-(4,6-dimethyl-2-pyrimidinyl)hydrazide and 6.18 g (13.89 mmol) of P_2S_5 in 60 mL of pyridine was heated at reflux for 1.5 h. After cooling, water was added and the reaction mixture was heated briefly at reflux to quench the reaction. The mixture was then cooled with an ice bath to precipitate the product. The solid was filtered and washed with water to give 6.57 g (21.73 mmol) of thiohydrazide which was then dissolved in 100 mL of THF with 7.5 mL (54.33 mmol) of triethylamine and 2.1 mL (23.91 mmol) of 1,2-dibromoethane. The reaction mixture was heated at reflux overnight. After cooling, water and ether were added and the organic phase was separated and washed with brine. The organic extracts were dried over magnesium sulfate, filtered and concentrated. The crude product was passed through a plug of silica gel to give 200 mg of product as an oil. ^{1}H NMR ($CDCl_3$), 7.8 (d, 2H), 7.2 (d, 2H), 6.53 (s, 1H), 4.45 (m, 2H), 3.35 (m, 2H), 2.67 (q, 2H), 2.41 (s, 6H), 1.22 (t, 3H).

EXAMPLE 5

Preparation of 4-(4,6-dimethyl-2-pyrimidinyl)-5,6-dihydro-2-(3-methylphenyl)-4H-1,3,4-oxadiazine

A solution of 1.00 g (3.89 mmol) of 3-methylbenzoic acid 2-(4,6-dimethyl-2-pyrimidinyl)hydrazide, 0.37 mL (4.28 mmol) of 1,2-dibromoethane, and 1.33 mL (8.95 mmol) of DBU in 20 mL of dry THF was heated at

reflux overnight. After cooling, 2.3 equivalents (8.95 mmol) of sodium hydride and 0.37 mL (4.28 mmol) of 1,2-dibromoethane were added, and the reaction mixture was heated at reflux overnight. The mixture was allowed to cool to room temperature and saturated aqueous ammonium chloride was added. The product was extracted with dichloromethane and chloroform and the organic phase was washed with brine. The organic extracts were dried over sodium sulfate, filtered, concentrated, and passed through a plug of silica gel to give 100 mg of desired product as a gum. ^{1}H NMR ($CDCl_3$) δ 7.82 (m, 1H), 7.75 (m, 1H), 7.25 (m, 1H), 7.19 (m, 1H), 6.49 (s, 1H), 4.54 (m, 2H), 4.28 (m, 2H), 2.42 (s, 6H), 2.38 (s, 3H).

EXAMPLE 6

Preparation of 4-methoxybenzenecarbothioic acid O-[2-(4,6-dimethyl-2-pyrimidinyl)hydrazide

4,6-Dimethyl-2-hydrazinopyrimidine (*p*-methoxythiobenzoylthio)acetic acid (2.00 g), 14.49 mmol) and *p*-methoxyphenylcarboxymethyldithioate (3.48 g, 14.4 mmol) were dissolved in 20 mL of 1N aqueous sodium hydroxide and 10 mL of water. The reaction mixture was stirred at 25°C for 16 h and then acidified with 1N HCl. The resultant precipitate was filtered, washed with water, and dried under vacuum to give 3.22 g (11.2 mmol, 78%) of the title hydrazide as a white solid, m.p. 212-215°C ^{1}H NMR ($CDCl_3$) δ 9.5 (bs, 1H), 7.85 (d, 2H), 6.95 (d, 2H), 6.57 (s, 1H), 3.87 (s, 3H), 2.39 (s, 6H).

EXAMPLE 7

Preparation of 4-(4,6-dimethyl-2-pyrimidinyl)-5,6-dihydro-2-phenyl-4H-1,3,4-thiadiazine

Benzenecarbothioic acid O-[2-(4,6-dimethyl-2-pyrimidinyl)]hydrazide (0.500 g, 1.94 mmol), triethylamine (4.85 mmol, 0.67 mL) and 1,2-dibromoethane (0.44 g, 2.33 mmol) were dissolved in

10 mL of THF and heated at reflux for 5 h. After cooling, water was added and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate, filtered and concentrated. The product was purified by flash chromatography on silica gel to yield 0.490 g (1.73 mmol) of a solid in 89% yield, m.p. 138-142°C. ^{1}H NMR ($CDCl_3$) δ 7.88 (m, 2H), 7.37 (m, 3H), 6.55 (s, 1H), 4.47 (m, 2H), 3.36 (m, 2H), 2.42 (s, 6H).

EXAMPLE 8

Preparation of 4-(4,6-dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine 1-oxide

4-(4,6-Dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine (0.800 g, 2.56 mmol) was dissolved in 10 mL of methanol and 2.5 mL of water. Sodium metaperiodate (0.600 g, 2.82 mmol) was added and the reaction mixture was heated at reflux for 1 h. Ethanol (2.5 mL) was added and heating was continued for 1 h more. The reaction mixture was then stirred at 25°C for 16 h. An additional 200 mg of sodium metaperiodate was added and the mixture was heated at reflux for 1 h. The reaction mixture was washed with water and extracted with methylene chloride. The organic layers were washed with brine, dried over sodium sulfate, and concentrated. The crude product was passed through a plug of silica gel to give 760 mg (91% yield) of a white solid, m.p. 149-164°C. ^{1}H NMR ($CDCl_3$) δ 7.95 (d, 2H), 7.28 (d, 2H), 6.7 (s, 1H), 5.45 (m, 1H), 3.9 (m, 1H), 3.4 (m, 1H), 2.85 (m, 1H), 2.7 (q, 2H), 2.49 (s, 6H), 1.26 (t, 3H).

EXAMPLE 9

Preparation of 4-(4,6-dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine 1,1-dioxide

4-(4,6-Dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine 1-oxide (0.350 g,

1.06 mmol) was dissolved in 5 mL of methanol and 2.5 mL of water. The mixture was cooled to 0°C and Oxone® (potassium peroxymonosulfate) (0.490 g, 0.80 mmol) was added. The reaction was warmed to room temperature, stirred for 1 h, then heated at reflux for 10 min. After stirring at 25°C for 16 h, water was added and the reaction mixture was extracted twice with methylene chloride. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated. The crude product was passed through a plug of silica gel to yield 350 mg (96%) of a white solid, m.p. 139-141°C. ^{1}H-NMR ($CDCl_3$) δ 7.90 (d, 2H), 7.27 (d, 2H), 6.72 (s, 1H), 5.05 (m, 2H), 3.55 (m, 2H), 2.67 (q, 2H), 2.47 (s, 6H), 1.24 (t, 3H).

EXAMPLE 10

Preparation of 4-(4,6-dimethyl-2-pyrimidinyl)-5,6-dihydro-2-phenoxy-4H-1,3,4-thiadiazine

O-Phenyl 2-(4,6-dimethyl-2-pyrimidinyl)hydrazinecarbothioate hydrochloride (4.00 g, 12.74 mmol) was dissolved in 38.5 mL of 1N aqueous sodium hydroxide, 40 mL of THF, and 1.31 mL (15.29 mmol) of 1,2-dibromoethane. The reaction mixture was stirred at 25°C for 4 days. Methylene chloride was added and the reaction was washed successively with water and brine. After drying over sodium sulfate and concentrating, the crude product was passed through a plug of silica gel to give 2.48 g (8.27 mmol, 65%) of a solid, m.p. 75-85°C. ^{1}H NMR ($CDCl_3$) δ 7.31 (m, 4H), 7.18 (m, 1H), 6.47 (s, 1H), 4.39 (m, 2H), 3.29 (m, 2H), 2.36 (s, 6H).

The compounds illustrated below are referred to in the tables which follow. G^1, G^2, G^3, X, Y, E and R^1-R^{28} are as defined for compounds of Formulae I-IV in the Summary of the Invention. In addition:

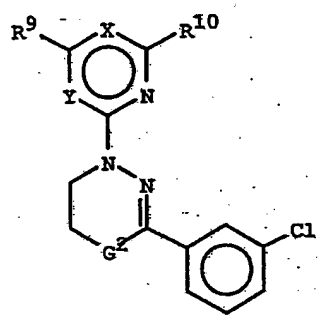
n = 0-2, as in the disclosure (e.g., Equation 2);

n^1 = 1-3;

n^2 = 0-1;

MCl_x = the metal chloride salts of copper, zinc, iron, magnesium, or manganese; and

x = 1-2.



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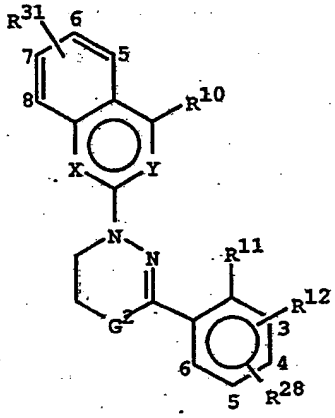

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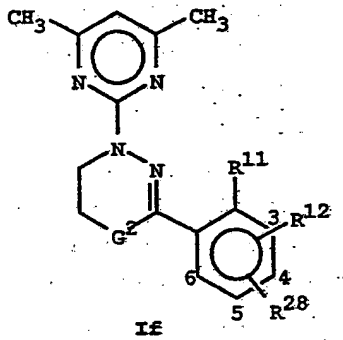

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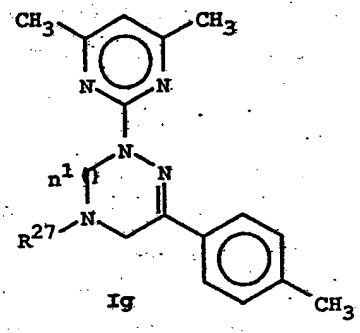

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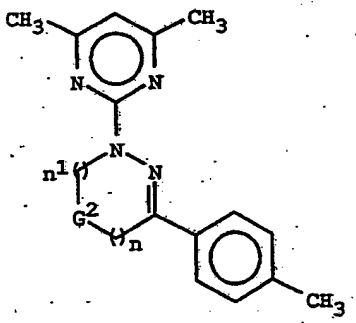

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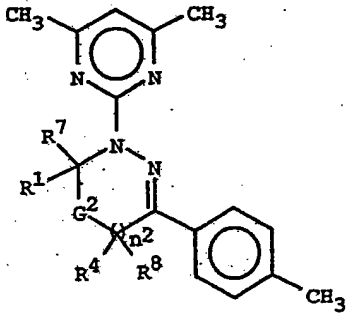

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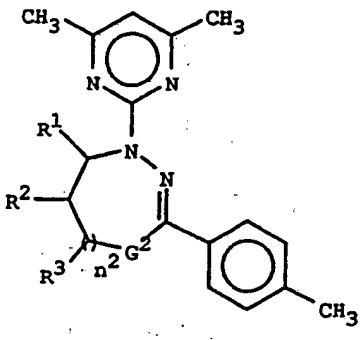

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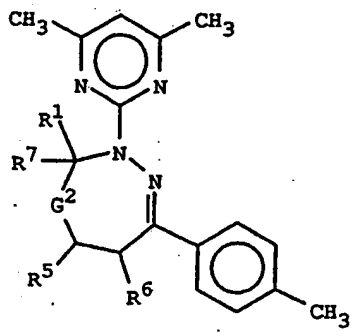

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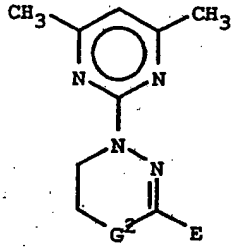

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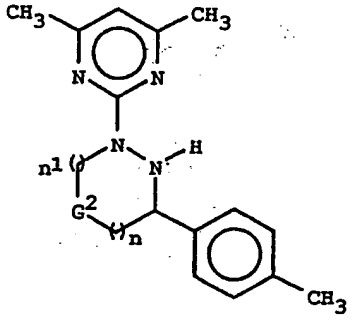

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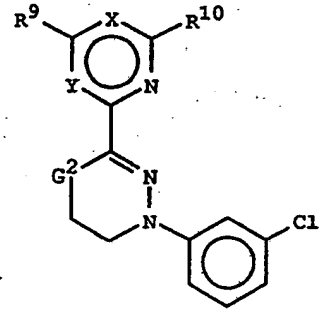

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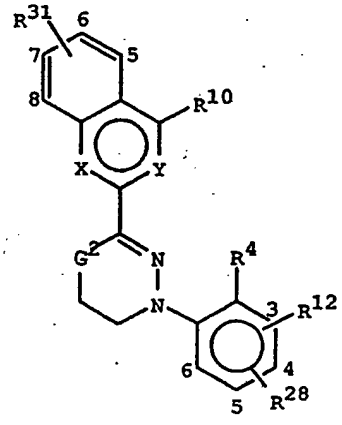

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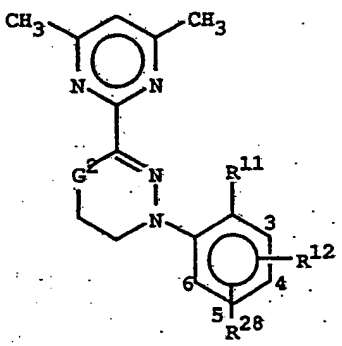

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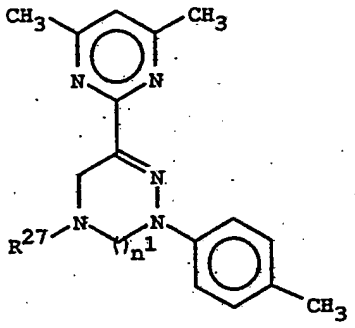

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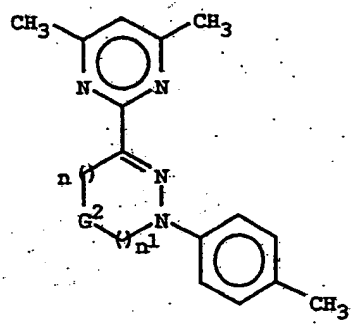

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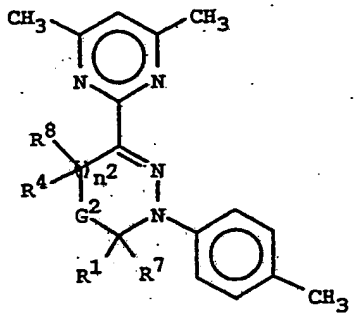

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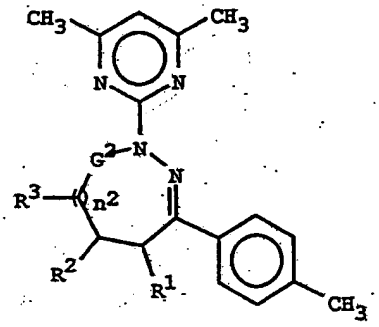

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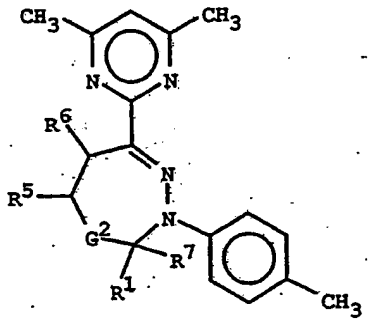

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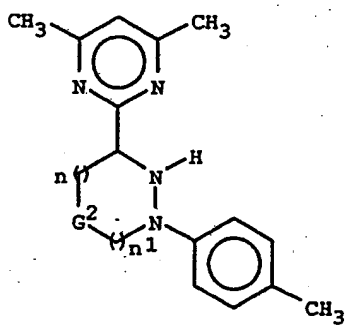

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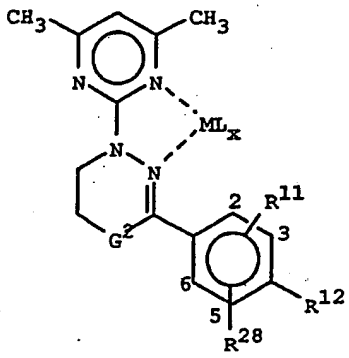


Im

The following abbreviations are used in the tables which follow. All alkyl groups are the normal isomers unless indicated otherwise.

t - is tertiary	t-Bu - is tertiary-butyl
s - is secondary	*c*-Pr - is cyclopropyl
n - is normal	*c*-Hex - is cyclohexyl
i - is iso	*s*-Bu - is secondary-butyl
c - is cyclo	OMe - is methoxy
Me - is methyl	*i*-PrO - is isopropoxy
Et - is ethyl	SEt - is ethylthio
Pr - is normal-propyl	CN - is cyano
Bu - is normal-butyl	TBS - is *t*-butyldimethylsilyl
Hex - is normal-hexyl	Ac - is acetyl
Ph - is phenyl	S(O)Me - is methylsulfinyl
Bzl - is benzyl	$S(O)_2Me$ - is methylsulfonyl
i-Pr - is isopropyl	

TABLE 1

Compounds of Formula Id

G^2=S, R^9=Me, Y=N, X=CH	$OCH_2CH=CH_2$	*i*-Pr
R^{10}	CH_2CH_2OMe	*c*-Pr
H	$OCHF_2$	*c*-Hex
Cl	C≡CH	2-Me-*c*-Pr
Br	$C\equiv CCH_2CH_3$	CF_3
F	$OCH_2C\equiv CH$	$(CH_2)_3CF_3$
CN	NH_2	SMe
OH	NMe_2	SBu
Me	NHEt	S(O)Me
Hex	4-morpholinyl	S(O)Bu
Et	pyrrolidinyl	$S(O)_2Me$
i-Pr	piperidinyl	$S(O)_2Bu$
c-Pr	Ph	OMe
c-Hex	PhO	OBu
2-Me-*c*-Pr	4-Me-Ph	OCH_2CF_3
CF_3	$3-CF_3$-Ph	$O(CH_2)_3CF_3$
$(CH_2)_3CF_3$	4-*i*-Pr-PhO	CH_2OMe
SMe	$4-F_2HCO$-Ph	$(CH_2)_3OMe$
SBu	3-Et-PhO	CH=CHMe
S(O)Me	4-MeO-PhO	$CH=CHCH_2CH_3$
S(O)Bu	4-MeO-Ph	$CH=CHCH_2CF_3$
$S(O)_2Me$		$CH=CCl_2$
$S(O)_2Bu$	G^2=O, R^9=Me, Y=N,	$OCH_2CH=CH_2$
OMe	X=CH	CH_2CH_2OMe
OBu	R^{10}	$OCHF_2$
OCH_2CF_3	H	C≡CH
$O(CH_2)_3CF_3$	Cl	$C\equiv CCH_2CH_3$
CH_2OMe	Br	$OCH_2C\equiv CH$
$(CH_2)_3OMe$	F	NH_2
CH=CHMe	CN	NMe_2
$CH=CHCH_2CH_3$	OH	NHEt
$CH=CHCH_2CF_3$	Me	4-morpholinyl
$CH=CCl_2$	Hex	pyrrolidinyl
	Et	piperidinyl

Ph
PhO
4-Me-Ph
3-CF_3-Ph
4-*i*-Pr-PhO
4-F_2HCO-Ph
3-Et-PhO
4-MeO-PhO
4-MeO-Ph

G^2=S, Y=N, X=CH,
R^{10}=H
R^9
H
Cl
Br
F
CN
OH
Me
Hex
Et
i-Pr
c-Pr
c-Hex
2-Me-*c*-Pr
CF_3
$(CH_2)_3CF_3$
SMe
SBu
S(O)Me
S(O)Bu
$S(O)_2Me$
$S(O)_2Bu$
OMe
OBu
OCH_2CF_3
$O(CH_2)_3CF_3$
CH_2OMe
$(CH_2)_3OMe$
CH=CHMe
$CH=CHCH_2CH_3$
$CH=CHCH_2CF_3$
$CH=CCl_2$
$OCH_2CH=CH_2$
CH_2CH_2OMe
$OCHF_2$
C≡CH
$C≡CCH_2CH_3$
$OCH_2C≡CH$
NH_2
NMe_2
NHEt
4-morpholinyl
pyrrolidinyl
piperidinyl
Ph
PhO
4-Me-Ph
3-CF_3-Ph
4-*i*-Pr-PhO
4-F_2HCO-Ph
3-Et-PhO
4-MeO-PhO
4-MeO-Ph

G^2=S, R^9=R^{10}=Me,
X=CR^{13}, Y=N
R^{13}
H
Cl
Br
F
CN
OH
Me
Hex
Et
i-Pr
c-Pr
c-Hex
2-Me-*c*-Pr
CF_3
$(CH_2)_3CF_3$
SMe
SBu
S(O)Me
S(O)Bu
$S(O)_2Me$
$S(O)_2Bu$
OMe
OBu
OCH_2CF_3
$O(CH_2)_3CF_3$
CH_2OMe
$(CH_2)_3OMe$
CH=CHMe
$CH=CHCH_2CH_3$
$CH=CHCH_2CF_3$
$CH=CCl_2$
$OCH_2CH=CH_2$
CH_2CH_2OMe
$OCHF_2$
C≡CH
$C≡CCH_2CH_3$

$OCH_2C{\equiv}CH$
NH_2
NMe_2
NHEt
4-morpholinyl
pyrrolidinyl
piperidinyl
Ph
PhO
4-Me-Ph
$3\text{-}CF_3\text{-}Ph$
4-*i*-Pr-PhO
$4\text{-}F_2HCO\text{-}Ph$
3-Et-PhO
4-MeO-PhO
4-MeO-Ph

$G^2{=}S$, $R^9{=}R^{10}{=}Me$,
$X{=}CH$, $Y{=}CR^{14}$
R^{14}
Cl
Br
F
Me
Et
OMe
OEt
H

$G^2{=}O$, $Y{=}N$, $X{=}CH$,
$R^{10}{=}H$
R^9
H
Cl
Br
F
CN
OH
Me
Hex
Et
i-Pr
c-Pr
c-Hex
2-Me-*c*-Pr
CF_3
$(CH_2)_3CF_3$
SMe
SBu
S(O)Me
S(O)Bu
$S(O)_2Me$
$S(O)_2Bu$
OMe
OBu
OCH_2CF_3
$O(CH_2)_3CF_3$
CH_2OMe
$(CH_2)_3OMe$
CH=CHMe
$CH{=}CHCH_2CH_3$
$CH{=}CHCH_2CF_3$
$CH{=}CCl_2$
$OCH_2CH{=}CH_2$
CH_2CH_2OMe
$OCHF_2$
$C{\equiv}CH$
$C{\equiv}CCH_2CH_3$
$OCH_2C{\equiv}CH$
NH_2
NMe_2
NHEt
4-morpholinyl
pyrrolidinyl
piperidinyl
Ph
PhO
4-Me-Ph
$3\text{-}CF_3\text{-}Ph$
4-*i*-Pr-PhO
$4\text{-}F_2HCO\text{-}Ph$
3-Et-PhO
4-MeO-PhO
4-MeO-Ph

$G^2{=}O$, $R^9{=}R^{10}{=}Me$,
$X{=}CR^{13}$, $Y{=}N$
R^{13}
H
Cl
Br
F
CN
OH
Me
Hex
Et
i-Pr
c-Pr
c-Hex
2-Me-*c*-Pr
CF_3
$(CH_2)_3CF_3$
SMe
SBu

S(O)Me
S(O)Bu
$S(O)_2Me$
$S(O)_2Bu$
OMe
OBu
OCH_2CF_3
$O(CH_2)_3CF_3$
CH_2OMe
$(CH_2)_3OMe$
CH=CHMe
$CH=CHCH_2CH_3$
$CH=CHCH_2CF_3$
$CH=CCl_2$
$OCH_2CH=CH_2$
CH_2CH_2OMe
$OCHF_2$
C≡CH
$C≡CCH_2CH_3$
$OCH_2C≡CH$
NH_2
NMe_2
NHEt
4-morpholinyl
pyrrolidinyl
piperidinyl
Ph
PhO
4-Me-Ph
$3-CF_3-Ph$
4-*i*-Pr-PhO
$4-F_2HCO-Ph$
3-Et-PhO
4-MeO-PhO
4-MeO-Ph

G^2=O, R^9=R^{10}=Me,
X=CH, Y=CR^{14}
R^{14}
Cl
Br
F
Me
Et
OMe
OEt
H

G^2=S, R^9=Me, X=Y=N
R^{10}
Cl
Br
F
CN
OH
Me
Et
i-Pr
c-Pr
CF_3
SMe
S(O)Me
$S(O)_2Me$
OMe
OEt
OCH_2OMe
OCH_2CF_3
C=CHMe
C≡CMe
NMe_2

Ph
PhO
4-Me-Ph
4-MeO-Ph
H

G^2=S, R^9=Me, Y=CH,
X=N
R^{10}
Cl
Br
F
CN
OH
Me
Et
i-Pr
c-Pr
CF_3
SMe
S(O)Me
$S(O)_2Me$
OMe
OEt
OCH_2OMe
OCH_2CF_3
C=CHMe
C≡CMe
NMe_2
Ph
PhO
4-Me-Ph
4-MeO-Ph
H

G^2=O, R^9=Me, X=Y=N	C=CHMe	*i*-Pr
R^{10}	C≡CMe	*c*-Pr
Cl	NMe_2	CF_3
Br	Ph	SMe
F	PhO	S(O)Me
CN	4-Me-Ph	$S(O)_2Me$
OH	4-MeO-Ph	OMe
Me	H	OEt
Et		OCH_2OMe
i-Pr	G^2=O, R^9=Me, Y=CH,	OCH_2CF_3
c-Pr	X=N	C=CHMe
CF_3	R^{10}	C≡CMe
SMe	Cl	NMe_2
S(O)Me	Br	Ph
$S(O)_2Me$	F	PhO
OMe	CN	4-Me-Ph
OEt	OH	4-MeO-Ph
OCH_2OMe	Me	H
OCH_2CF_3	Et	

G^2=S

X	Y	R^{14}	R^9	R^{13}	R^{10}
N	CR^{14}	$-(CH_2)_3-$		—	Me
CH	CR^{14}	$-(CH_2)_3-$		—	Me
N	CR^{14}	$-(CH_2)_4-$		—	Me
CH	CR^{14}	$-(CH_2)_4-$		—	Me
CR^{13}	N	—	$-(CH_2)_3-$		Me
CR^{13}	CH	—	$-(CH_2)_3-$		Me
CR^{13}	N	—	$-(CH_2)_4-$		Me
CR^{13}	CH	—	$-(CH_2)_4-$		Me
CR^{13}	CH	—	Me	$-(CH_2)_3-$	
CR^{13}	CH	—	Me	$-(CH_2)_4-$	

G^2=O

X	Y	R^{14}	R^9	R^{13}	R^{10}
N	CR^{14}	$-(CH_2)_3-$		--	Me
CH	CR^{14}	$-(CH_2)_3-$		--	Me
N	CR^{14}	$-(CH_2)_4-$		--	Me
CH	CR^{14}	$-(CH_2)_4-$		--	Me
CR^{13}	N	--	$-(CH_2)_3-$		Me
CR^{13}	CH	--	$-(CH_2)_3-$		Me
CR^{13}	N	--	$-(CH_2)_4-$		Me
CR^{13}	CH	--	$-(CH_2)_4-$		Me
CR^{13}	CH	--	Me	$-(CH_2)_3-$	
CR^{13}	CH	--	Me	$-(CH_2)_4-$	

TABLE 2

Compounds of Formula Ie

G^2=S, X=Y=N, R^{11}=R^{12}=R^{28}=H

R^{10}	c-Pr	C=CHMe
Cl	CF_3	C=CMe
Br	SMe	NMe_2
F	S(O)Me	Ph
CN	$S(O)_2Me$	PhO
OH	OMe	4-Me-Ph
Me	OEt	4-MeO-Ph
Et	OCH_2OMe	H
i-Pr	OCH_2CF_3	

G^2=S

X	Y	R^{10}	R^{11}	R^{12}	R^{28}	R^{31}
CH	N	Me	H	H	H	H
N	CH	Me	H	H	H	H
N	N	Me	H	3-Me	4-Me	H
N	N	Me	H	3-Me	4-Me	6-Me
N	N	Me	Me	H	H	7-Me

N	N	Me	H	H	4-*i*-Pr	6-OMe
N	N	Me	H	3-Me	H	7-CF_3
N	N	Me	H	H	4-Et	7-Et
N	N	Me	H	H	4-*i*-Pr	6-$OCHF_2$
N	N	Me	H	H	H	8-Bu
N	N	Me	H	H	4-*c*-Pr	6-OEt

G^2=O, X=Y=N, R^{11}=R^{12}=R^{28}=H

R^{10}			
Cl	*c*-Pr	C≡CHMe	
Br	CF_3	C≡CMe	
F	SMe	NMe_2	
CN	S(O)Me	Ph	
OH	$S(O)_2Me$	PhO	
Me	OMe	4-Me-Ph	
Et	OEt	4-MeO-Ph	
i-Pr	OCH_2OMe	H	
	OCH_2CF_3		

G^2=O

X	Y	R^{10}	R^{11}	R^{12}	R^{28}	R^{31}
CH	N	Me	H	H	H	H
N	CH	Me	H	H	H	H
N	N	Me	H	3-Me	4-Me	H
N	N	Me	H	3-Me	4-Me	6-Me
N	N	Me	Me	H	H	7-Me
N	N	Me	H	H	4-*i*-Pr	6-OMe
N	N	Me	H	3-Me	H	7-CF_3
N	N	Me	H	H	4-Et	7-Et
N	N	Me	H	H	4-*i*-Pr	6-$OCHF_2$
N	N	Me	H	H	H	8-Bu
N	N	Me	H	H	4-*c*-Pr	6-OEt

TABLE 3

Compounds of Formula If

G^2=S, R^{12}=H, R^{28}=H	G^2=S, R^{11}=R^{12}=H	4-C≡CH
R^{11}	R^{28}	4-C≡C-Et
H	4-Me	4-$OCH_2C{\equiv}CH$
Me	4-CN	4-NMe_2
Et	4-NO_2	4-C(=O)NMe_2
i-Pr	4-OH	4-Ph
s-Bu	4-CO_2H	4-OPh
F	4-CO_2Et	4-SPh
Cl	4-Et	4-(3-Me-Ph)
Br	4-*i*-Pr	
CF_3	4-*n*-Hex	G^2=S
OMe	4-*c*-Pr	R^{11} R^{12} R^{28}
OEt	4-CF_3	Cl H 6-Cl
$OCHF_2$	4-SMe	H 3-Me 4-Me
OBu	4-SBu	H 3-Me 4-Et
$O(CH_2)_3CF_3$	4-*c*-Hex	H 3-OMe 4-OMe
$(CH_2)_3CF_3$	4-Cl	Me H 5-Me
G^2=S, R^{11}=H, R^{28}=H	4-Br	Me H 4-Me
R^{12}	4-F	Me 4-Me 5-Me
3-Me	4-$(CH_2)_3CF_3$	H 3-Cl 5-Cl
3-Et	4-S(O)Me	Cl H 4-Cl
3-*i*-Pr	4-S(O)Bu	
3-*s*-Bu	4-$S(O)_2Me$	G^2=O, R^{12}=H, R^{28}=H
3-F	4-$S(O)_2Bu$	R^{11}
3-Cl	4-OMe	H
3-Br	4-OBu	Me
3-CF_3	4-OCH_2CF_3	Et
3-OMe	4-OCH_2OMe	*i*-Pr
3-OEt	4-CH_2OMe	*s*-Bu
3-$OCHF_2$	4-CH=CH-Me	F
3-OBu	4-$CH{=}CHCH_2Me$	Cl
3-$O(CH_2)_3CF_3$	4-TBS	Br
3-$(CH_2)_3CF_3$	4-$SiMe_3$	CF_3

OMe
OEt
$OCHF_2$
OBu
$O(CH_2)_3CF_3$
$(CH_2)_3CF_3$

G^2=O, R^{11}=H, R^{28}=H
R^{12}
3-Me
3-Et
3-*i*-Pr
3-*s*-Bu
3-F
3-Cl
3-Br
$3-CF_3$
3-OMe
3-OEt
$3-OCHF_2$
3-OBu
$3-O(CH_2)_3CF_3$
$3-(CH_2)_3CF_3$

G^2=O, R^{11}=R^{12}=H
R^{28}
4-Me
4-CN
$4-NO_2$
4-OH
$4-CO_2H$
$4-CO_2Et$
4-Et
4-*i*-Pr
4-*n*-Hex
4-*c*-Pr
$4-CF_3$
4-SMe
4-SBu
4-*c*-Hex
4-Cl
4-Br
4-F
$4-(CH_2)_3CF_3$
4-S(O)Me
4-S(O)Bu
$4-S(O)_2Me$
$4-S(O)_2Bu$
4-OMe
4-OBu
$4-OCH_2CF_3$
$4-OCH_2OMe$
$4-CH_2OMe$
4-CH=CH-Me
$4-CH=CHCH_2Me$
4-TBS
$4-SiMe_3$
4-C≡CH
4-C≡C-Et
$4-OCH_2C≡CH$
$4-NMe_2$
$4-C(=O)NMe_2$
4-Ph
4-OPh
4-SPh
4-(3-Me-Ph)

G^2=O

R^{11}	R^{12}	R^{28}
Cl	H	6-Cl
H	3-Me	4-Me
H	3-Me	4-Et
H	3-OMe	4-OMe
Me	H	5-Me
Me	H	4-Me
Me	4-Me	5-Me
H	3-Cl	5-Cl
Cl	H	4-Cl

G^2=S(O), R^{12}=H,
R^{28}=H
R^{11}
H
Me
Et
i-Pr
s-Bu
F
Cl
Br
CF_3
OMe
OEt
$OCHF_2$
OBu
$O(CH_2)_3CF_3$
$(CH_2)_3CF_3$

G^2=S(O), R^{11}=H,
R^{28}=H
R^{12}
3-Me
3-Et
3-*i*-Pr
3-*s*-Bu

3-F
3-Cl
3-Br
3-CF_3
3-OMe
3-OEt
3-$OCHF_2$
3-OBu
3-$O(CH_2)_3CF_3$
3-$(CH_2)_3CF_3$

G^2=S(O), R^{11}=R^{12}=H

R^{28}

4-Me
4-CN
4-NO_2
4-OH
4-CO_2H
4-CO_2Et
4-Et
4-*i*-Pr
4-*n*-Hex
4-*c*-Pr
4-CF_3
4-SMe
4-SBu
4-*c*-Hex
4-Cl
4-Br
4-F
4-$(CH_2)_3CF_3$
4-S(O)Me
4-S(O)Bu
4-$S(O)_2Me$
4-$S(O)_2Bu$
4-OMe
4-OBu
4-OCH_2CF_3
4-OCH_2OMe
4-CH_2OMe
4-CH=CH-Me
4-$CH=CHCH_2Me$
4-TBS
4-$SiMe_3$
4-C≡CH
4-C≡C-Et
4-$OCH_2C≡CH$
4-NMe_2
4-C(=O)NMe_2
4-Ph
4-OPh
4-SPh
4-(3-Me-Ph)

G^2=S(O)

R^{11}	R^{12}	R^{28}
Cl	H	6-Cl
H	3-Me	4-Me
H	3-Me	4-Et
H	3-OMe	4-OMe
Me	H	5-Me
Me	H	4-Me
Me	4-Me	5-Me
H	3-Cl	5-Cl
Cl	H	4-Cl

G^2=$S(O)_2$, R^{12}=H,

R^{28}=H

R^{11}

H
Me
Et
i-Pr
s-Bu
F
Cl
Br
CF_3
OMe
OEt
$OCHF_2$
OBu
$O(CH_2)_3CF_3$
$(CH_2)_3CF_3$

G^2=$S(O)_2$, R^{11}=H,

R^{28}=H

R^{12}

3-Me
3-Et
3-*i*-Pr
3-*s*-Bu
3-F
3-Cl
3-Br
3-CF_3
3-OMe
3-OEt
3-$OCHF_2$
3-OBu
3-$O(CH_2)_3CF_3$
3-$(CH_2)_3CF_3$

G^2=S(O)$_2$,
R^{11}=R^{12}=H

R^{28}
4-Me
4-CN
4-NO_2
4-OH
4-CO_2H
4-CO_2Et
4-Et
4-*i*-Pr
4-*n*-Hex
4-*c*-Pr
4-CF_3
4-SMe
4-SBu
4-*c*-Hex
4-Cl
4-Br
4-F
4-$(CH_2)_3CF_3$
4-S(O)Me
4-S(O)Bu
4-S(O)$_2$Me
4-S(O)$_2$Bu
4-OMe
4-OBu
4-OCH_2CF_3
4-OCH_2OMe
4-CH_2OMe
4-CH=CH-Me
4-CH=$CHCH_2$Me
4-TBS
4-$SiMe_3$
4-C≡CH
4-C≡C-Et
4-OCH_2C≡CH
4-NMe_2
4-C(=O)NMe_2
4-Ph
4-OPh
4-SPh
4-(3-Me-Ph)

G^2=S(O)$_2$

R^{11}	R^{12}	R^{28}
Cl	H	6-Cl
H	3-Me	4-Me
H	3-Me	4-Et
H	3-OMe	4-OMe
Me	H	5-Me
Me	H	4-Me
Me	4-Me	5-Me
H	3-Cl	5-Cl
Cl	H	4-Cl

TABLE 4

Compounds of Formula Ig

n^1=1	
R^{27}	
H	
Et	
Bu	
i-Pr	
CHF_2	
$(CH_2)_3CF_3$	
CO_2Et	
C(=O)Me	
C(=O)$(CH_2)_3$Me	
C(=O)Ph	
(3-Me-Ph)C(=O)	
(4-OMe-Ph)C(=O)	
$CH_2C{=}CH_2$	
$CH_2C{\equiv}CH$	
$PhCH_2$	
4-Me-$PhCH_2$	
S(=O)$_2$Me	
C(=O)NMe_2	
C(=S)NHMe	
S(O)Me	
S(O)$_2$Ph	
(4-Me-Ph)S(O)$_2$	
C(=O)NHPh	
C(=S)NHPh	
P(=S)$(OEt)_2$	
P(=O)$(OEt)_2$	
S(O)$_2$N$(Et)_2$	
n^1=2	
R^{27}	
H	
Et	
Bu	
i-Pr	
CHF_2	
$(CH_2)_3CF_3$	
CO_2Et	
C(=O)Me	
C(=O)$(CH_2)_3$Me	
C(=O)Ph	
(3-Me-Ph)C(=O)	
(4-OMe-Ph)C(=O)	
$CH_2C{=}CH_2$	
$CH_2C{\equiv}CH$	
$PhCH_2$	
4-Me-$PhCH_2$	
S(O)$_2$Me	
C(=O)NMe_2	
C(=S)NHMe	
S(O)Me	
S(O)$_2$Ph	
(4-Me-Ph)S(O)$_2$	
C(=O)NHPh	
C(=S)NHPh	
P(=S)$(OEt)_2$	
P(=O)$(OEt)_2$	
S(O)$_2$N$(Et)_2$	
n^1=3	
R^{27}	
H	
Et	
Bu	
i-Pr	

CHF_2
$(CH_2)_3CF_3$
CO_2Et
C(=O)Me
$C(=O)(CH_2)_3Me$
C(=O)Ph
(3-Me-Ph)C(=O)
(4-OMe-Ph)C(=O)
$CH_2C=CH_2$
$CH_2C\equiv CH$
$PhCH_2$
4-Me-$PhCH_2$
$S(O)_2Me$
$C(=O)NMe_2$
C(=S)NHMe
S(O)Me
$S(O)_2Ph$
(4-Me-Ph)$S(O)_2$
C(=O)NHPh
C(=S)NHPh
$P(=S)(OEt)_2$
$P(=O)(OEt)_2$
$S(O)_2N(Et)_2$

TABLE 5

Compounds of Formula Ih

n	n^1	G^2
1	1	S
1	2	S
2	1	S
0	3	S
1	1	O
1	2	O
2	1	O
0	3	O
1	1	S(O)
1	2	S(O)
2	1	S(O)
0	3	S(O)
1	1	$S(O)_2$
1	2	$S(O)_2$
2	1	$S(O)_2$
0	3	$S(O)_2$
1	1	N-Me
1	2	N-Me
2	1	N-Me

TABLE 6

Compounds of Formula Ii

G^2=S

n^2	R^1	R^7	R^4	R^8
1	Me	H	H	H
1	Bu	H	H	H
1	Me	Me	H	H
1	H	H	Me	H
1	H	H	Bu	H
1	Ph	H	H	H
1	4-Me-Ph	H	H	H
1	4-OMe-Ph	H	H	H
0	Me	H	--	--
0	Bu	H	--	--
0	Me	Me	--	--
0	Ph	H	--	--
0	4-Me-Ph	H	--	--

G^2=O

n^2	R^1	R^7	R^4	R^8
1	Me	H	H	H
1	Bu	H	H	H
1	Me	Me	H	H

1	H	H	Me	H
1	H	H	Bu	H
1	Ph	H	H	H
1	4-Me-Ph	H	H	H
1	4-OMe-Ph	H	H	H
0	Me	H	--	--
0	Bu	H	--	--
0	Me	Me	--	--
0	Ph	H	--	--
0	4-Me-Ph	H	--	--

TABLE 7

Compounds of Formula Ij

G^2=S

n^2	R^1	R^2	R^3
0	Me	H	--
0	Bu	H	--
0	H	Me	--
0	H	Bu	--
0	Ph	H	--
0	4-Me-Ph	H	--
0	H	4-OMe-Ph	--
1	Me	H	H
1	Bu	H	H
1	H	Me	H
1	H	Bu	H
1	H	H	Me
1	H	H	Bu
1	Ph	H	H
1	4-Me-Ph	H	H
1	H	Ph	H
1	H	4-Me-Ph	H
1	H	H	Ph
1	H	H	4-Me-Ph

G^2=O

n^2	R^1	R^2	R^3
0	Me	H	--
0	Bu	H	--
0	H	Me	--
0	H	Bu	--
0	Ph	H	--
0	4-Me-Ph	H	--
0	H	4-OMe-Ph	--
1	Me	H	H
1	Bu	H	H

n^2	R^1	R^2	R^3
1	H	Me	H
1	H	Bu	H
1	H	H	Me
1	H	H	Bu
1	Ph	H	H

n^2	R^1	R^2	R^3
1	4-Me-Ph	H	H
1	H	Ph	H
1	H	4-Me-Ph	H
1	H	H	Ph
1	H	H	4-Me-Ph

TABLE 8

Compounds of Formula Ik

G^2=S

R^1	R^7	R^5	R^6
H	H	Me	H
H	H	Ph	H
H	H	H	Me
H	H	H	Ph

Me	H	H	H
Me	Me	H	H
Ph	H	H	H
H	Ph	H	H
H	H	Bu	H
H	H	4-Me-Ph	H
H	H	H	Bu
H	H	H	4-OMe-Ph
Bu	H	H	H
3-Me-Ph	H	H	H
4-OMe-Ph	H	H	H

Ph	H	H	H
H	Ph	H	H
H	H	Bu	H
H	H	4-Me-Ph	H
H	H	H	Bu
H	H	H	4-OMe-Ph
Bu	H	H	H
3-Me-Ph	H	H	H
4-OMe-Ph	H	H	H

G^2=O

R^1	R^7	R^5	R^6
H	H	Me	H
H	H	Ph	H
H	H	H	Me
H	H	H	Ph
Me	H	H	H
Me	Me	H	H

TABLE 9

Compounds of Formula Il

G^2=S	3-thienyl
E	2,5-diMe-3-furanyl
H	2,5-diMe-3-thienyl
Me	4-Me-PhO
n-Hex	2-Cl-PhO
c-Hex	2,6-diMe-PhO
$PhCH_2$	4-Me-PhNH
$CH_2CH_2CF_3$	3-Me-PhS
OBu	*s*-BuS
$O(CH_2)_5Cl$	1-indanyl
1-naphthalenyl	5-Me-2-thienyl
2-naphthalenyl	5-Me-2-pyridyl
2-furanyl	4-Me-3-furanyl

2-Me-3-pyridyl

G^2=O

E

H

Me

n-Hex

c-Hex

$PhCH_2$

$CH_2CH_2CF_3$

OBu

$O(CH_2)_5Cl$

1-naphthalenyl

2-naphthalenyl

2-furanyl

3-thienyl

2,5-diMe-3-furanyl

2,5-diMe-3-thienyl

4-Me-PhO

2-Cl-PhO

2,6-diMe-PhO

4-Me-PhNH

3-Me-PhS

s-BuS

1-indanyl

5-Me-2-thienyl

5-Me-2-pyridyl

4-Me-3-furanyl

2-Me-3-pyridyl

G^2=S(O)

E

H

Me

n-Hex

c-Hex

$PhCH_2$

$CH_2CH_2CF_3$

OBu

$O(CH_2)_5Cl$

1-naphthalenyl

2-naphthalenyl

2-furanyl

3-thienyl

2,5-diMe-3-furanyl

2,5-diMe-3-thienyl

4-Me-PhO

2-Cl-PhO

2,6-diMe-PhO

4-Me-PhNH

3-Me-PhS

s-BuS

1-indanyl

5-Me-2-thienyl

5-Me-2-pyridyl

4-Me-3-furanyl

2-Me-3-pyridyl

G^2=$S(O)_2$

E

H

Me

n-Hex

c-Hex

$PhCH_2$

$CH_2CH_2CF_3$

OBu

$O(CH_2)_5Cl$

1-naphthalenyl

2-naphthalenyl

2-furanyl	3-Me-PhS
3-thienyl	*s*-BuS
2,5-diMe-3-furanyl	1-indanyl
2,5-diMe-3-thienyl	5-Me-2-thienyl
4-Me-PhO	5-Me-2-pyridyl
2-Cl-PhO	4-Me-3-furanyl
2,6-diMe-PhO	2-Me-3-pyridyl
4-Me-PhNH	

TABLE 10

Compounds of formula IIIc

G^2	n	n^1			
S	0	1	S(O)	1	1
S	0	2	S(O)	1	2
S	0	3	S(O)	2	1
S	1	1	$S(O)_2$	0	1
S	1	2	$S(O)_2$	0	2
S	2	1	$S(O)_2$	0	3
O	0	1	$S(O)_2$	1	1
O	0	2	$S(O)_2$	1	2
O	0	3	$S(O)_2$	2	1
O	1	1	NMe	0	1
O	1	2	NMe	0	2
O	2	1	NMe	0	3
S(O)	0	1	NMe	1	1
S(O)	0	2	NMe	1	2
S(O)	0	3	NMe	2	1

TABLE 11

Compounds of Formula IIc

G^2=S, R^9=Me, Y=N,		
X=CH	Br	Hex
R^{10}	F	Et
H	CN	*i*-Pr
Cl	OH	*c*-Pr
	Me	*c*-Hex

2-Me-*c*-Pr
CF_3
$(CH_2)_3CF_3$
SMe
SBu
S(O)Me
S(O)Bu
$S(O)_2Me$
$S(O)_2Bu$
OMe
OBu
OCH_2CF_3
$O(CH_2)_3CF_3$
CH_2OMe
$(CH_2)_3OMe$
CH=CHMe
$CH=CHCH_2CH_3$
$CH=CHCH_2CF_3$
$CH=CCl_2$
$OCH_2CH=CH_2$
CH_2CH_2OMe
$OCHF_2$
C≡CH
$C≡CCH_2CH_3$
$OCH_2C≡CH$
NH_2
NMe_2
NHEt
4-morpholinyl
pyrrolidinyl
piperidinyl
Ph
PhO
4-Me-Ph
$3-CF_3-Ph$

4-*i*-Pr-PhO
$4-F_2HCO-Ph$
3-Et-PhO
4-MeO-PhO
4-MeO-Ph

G^2=O, R^9=Me, Y=N,
X=CH
R^{10}
H
Cl
Br
F
CN
OH
Me
Hex
Et
i-Pr
c-Pr
c-Hex
2-Me-*c*-Pr
CF_3
$(CH_2)_3CF_3$
SMe
SBu
S(O)Me
S(O)Bu
$S(O)_2Me$
$S(O)_2Bu$
OMe
OBu
OCH_2CF_3
$O(CH_2)_3CF_3$
CH_2OMe

$(CH_2)_3OMe$
CH=CHMe
$CH=CHCH_2CH_3$
$CH=CHCH_2CF_3$
$CH=CCl_2$
$OCH_2CH=CH_2$
CH_2CH_2OMe
$OCHF_2$
C≡CH
$C≡CCH_2CH_3$
$OCH_2C≡CH$
NH_2
NMe_2
NHEt
4-morpholinyl
pyrrolidinyl
piperidinyl
Ph
PhO
4-Me-Ph
$3-CF_3-Ph$
4-*i*-Pr-PhO
$4-F_2HCO-Ph$
3-Et-PhO
4-MeO-PhO
4-MeO-Ph

G^2=S, Y=N, X=CH,
R^{10}=H
R^9
H
Cl
Br
F
CN

OH
Me
Hex
Et
i-Pr
c-Pr
c-Hex
2-Me-*c*-Pr
CF_3
$(CH_2)_3CF_3$
SMe
SBu
S(O)Me
S(O)Bu
$S(O)_2Me$
$S(O)_2Bu$
OMe
OBu
OCH_2CF_3
$O(CH_2)_3CF_3$
CH_2OMe
$(CH_2)_3OMe$
CH=CHMe
$CH=CHCH_2CH_3$
$CH=CHCH_2CF_3$
$CH=CCl_2$
$OCH_2CH=CH_2$
CH_2CH_2OMe
$OCHF_2$
C≡CH
$C\equiv CCH_2CH_3$
$OCH_2C\equiv CH$
NH_2
NMe_2
NHEt
4-morpholinyl
pyrrolidinyl
piperidinyl
Ph
PhO
4-Me-Ph
$3\text{-}CF_3\text{-}Ph$
4-*i*-Pr-PhO
$4\text{-}F_2HCO\text{-}Ph$
3-Et-PhO
4-MeO-PhO
4-MeO-Ph

G^2=S, R^9=R^{10}=Me,
X=CR^{13}, Y=N
R^{13}
H
Cl
Br
F
CN
OH
Me
Hex
Et
i-Pr
c-Pr
c-Hex
2-Me-*c*-Pr
CF_3
$(CH_2)_3CF_3$
SMe
SBu
S(O)Me
S(O)Bu
$S(O)_2Me$
$S(O)_2Bu$
OMe
OBu
OCH_2CF_3
$O(CH_2)_3CF_3$
CH_2OMe
$(CH_2)_3OMe$
CH=CHMe
$CH=CHCH_2CH_3$
$CH=CHCH_2CF_3$
$CH=CCl_2$
$OCH_2CH=CH_2$
CH_2CH_2OMe
$OCHF_2$
C≡CH
$C\equiv CCH_2CH_3$
$OCH_2C\equiv CH$
NH_2
NMe_2
NHEt
4-morpholinyl
pyrrolidinyl
piperidinyl
Ph
PhO
4-Me-Ph
$3\text{-}CF_3\text{-}Ph$
4-*i*-Pr-PhO
$4\text{-}F_2HCO\text{-}Ph$
3-Et-PhO
4-MeO-PhO
4-MeO-Ph

G^2=S, R^9=R^{10}=Me, X=CH, Y=CR^{14}

R^{14}

Cl

Br

F

Me

Et

OMe

OEt

H

G^2=O, Y=N, X=CH, R^{10}=H

R^9

H

Cl

Br

F

CN

OH

Me

Hex

Et

i-Pr

c-Pr

c-Hex

2-Me-*c*-Pr

CF_3

$(CH_2)_3CF_3$

SMe

SBu

S(O)Me

S(O)Bu

$S(O)_2Me$

$S(O)_2Bu$

OMe

OBu

OCH_2CF_3

$O(CH_2)_3CF_3$

CH_2OMe

$(CH_2)_3OMe$

CH=CHMe

$CH=CHCH_2CH_3$

$CH=CHCH_2CF_3$

$CH=CCl_2$

$OCH_2CH=CH_2$

CH_2CH_2OMe

$OCHF_2$

C≡CH

$C≡CCH_2CH_3$

$OCH_2C≡CH$

NH_2

NMe_2

NHEt

4-morpholinyl

pyrrolidinyl

piperidinyl

Ph

PhO

4-Me-Ph

3-CF_3-Ph

4-*i*-Pr-PhO

4-F_2HCO-Ph

3-Et-PhO

4-MeO-PhO

4-MeO-Ph

G^2=O, R^9=R^{10}=Me, X=CR^{13}, Y=N

R^{13}

H

Cl

Br

F

CN

OH

Me

Hex

Et

i-Pr

c-Pr

c-Hex

2-Me-*c*-Pr

CF_3

$(CH_2)_3CF_3$

SMe

SBu

S(O)Me

S(O)Bu

$S(O)_2Me$

$S(O)_2Bu$

OMe

OBu

OCH_2CF_3

$O(CH_2)_3CF_3$

CH_2OMe

$(CH_2)_3OMe$

CH=CHMe

$CH=CHCH_2CH_3$

$CH=CHCH_2CF_3$

$CH=CCl_2$

$OCH_2CH=CH_2$

CH_2CH_2OMe

$OCHF_2$

C≡CH
C≡CCH$_2$CH$_3$
OCH$_2$C≡CH
NH$_2$
NMe$_2$
NHEt
4-morpholinyl
pyrrolidinyl
piperidinyl
Ph
PhO
4-Me-Ph
3-CF$_3$-Ph
4-*i*-Pr-PhO
4-F$_2$HCO-Ph
3-Et-PhO
4-MeO-PhO
4-MeO-Ph

G^2=O, R^9=R^{10}=Me, X=CH, Y=CR^{14}

R^{14}
Cl
Br
F
Me
Et
OMe
OEt
H

G^2=S, R^9=Me, X=Y=N

R^{10}
Cl
Br
F
CN
OH
Me
Et
i-Pr
c-Pr
CF$_3$
SMe
S(O)Me
S(O)$_2$Me
OMe
OEt
OCH$_2$OMe
OCH$_2$CF$_3$
C=CHMe
C≡CMe
NMe$_2$
Ph
PhO
4-Me-Ph
4-MeO-Ph
H

G^2=S, R^9=Me, Y=CH, X=N

R^{10}
Cl
Br
F
CN
OH
Me
Et
i-Pr
c-Pr
CF$_3$
SMe
S(O)Me
S(O)$_2$Me
OMe
OEt
OCH$_2$OMe
OCH$_2$CF$_3$
C=CHMe
C≡CMe
NMe$_2$
Ph
PhO
4-Me-Ph
4-MeO-Ph
H

G^2=O, R^9=Me, X=Y=N

R^{10}
Cl
Br
F
CN
OH
Me
Et
i-Pr
c-Pr
CF$_3$
SMe
S(O)Me
S(O)$_2$Me
OMe
OEt

OCH_2OMe	Cl	OEt
OCH_2CF_3	Br	OCH_2OMe
C=CHMe	F	OCH_2CF_3
C≡CMe	CN	C=CHMe
NMe_2	OH	C≡CMe
Ph	Me	NMe_2
PhO	Et	Ph
4-Me-Ph	*i*-Pr	PhO
4-MeO-Ph	*c*-Pr	4-Me-Ph
H	CF_3	4-MeO-Ph
	SMe	H
G^2=O, R^9=Me, Y=CH,	S(O)Me	
X=N	$S(O)_2Me$	
R^{10}	OMe	

G^2=S

X	Y	R^{14}	R^9	R^{13}	R^{10}
N	CR^{14}	$-(CH_2)_3-$		--	Me
CH	CR^{14}	$-(CH_2)_3-$		--	Me
N	CR^{14}	$-(CH_2)_4-$		--	Me
CH	CR^{14}	$-(CH_2)_4-$		--	Me
CR^{13}	N	--	$-(CH_2)_3-$		Me
CR^{13}	CH	--	$-(CH_2)_3-$		Me
CR^{13}	N	--	$-(CH_2)_4-$		Me
CR^{13}	CH	--	$-(CH_2)_4-$		Me
CR^{13}	CH	--	Me	$-(CH_2)_3-$	
CR^{13}	CH	--	Me	$-(CH_2)_4-$	

G^2=O

X	Y	R^{14}	R^9	R^{13}	R^{10}
N	CR^{14}	$-(CH_2)_3-$		--	Me
CH	CR^{14}	$-(CH_2)_3-$		--	Me
N	CR^{14}	$-(CH_2)_4-$		--	Me
CH	CR^{14}	$-(CH_2)_4-$		--	Me
CR^{13}	N	--	$-(CH_2)_3-$		Me

CR^{13}	CH	--	$-(CH_2)_3-$		Me
CR^{13}	N	--	$-(CH_2)_4-$		Me
CR^{13}	CH	--	$-(CH_2)_4-$		Me
CR^{13}	CH	--	Me	$-(CH_2)_3-$	
CR^{13}	CH	--	Me	$-(CH_2)_4-$	

TABLE 12

Compounds of Formula IId

G^2=S, X=Y=N, R^{11}=R^{12}=R^{28}=H

R^{10}		
Cl	c-Pr	C=CHMe
Br	CF_3	C≡CMe
F	SMe	NMe_2
CN	S(O)Me	Ph
OH	$S(O)_2Me$	PhO
Me	OMe	4-Me-Ph
Et	OEt	4-MeO-Ph
i-Pr	OCH_2OMe	H
	OCH_2CF_3	

G^2=S, R^{10}=Me

X	Y	R^{11}	R^{12}	R^{28}	R^{31}
CH	N	H	H	H	H
N	CH	H	H	H	H
N	N	H	3-Me	4-Me	H
N	N	H	3-Me	4-Me	6-Me
N	N	Me	H	H	7-Me
N	N	H	H	4-i-Pr	6-OMe
N	N	H	3-Me	H	$7-CF_3$
N	N	H	H	4-Et	7-Et
N	N	H	H	4-i-Pr	$6-OCHF_2$
N	N	H	H	H	8-Bu
N	N	H	H	4-c-Pr	6-OEt

G^2=O, X=Y=N, R^{11}=R^{12}=R^{28}=H

R^{10}		
Cl	c-Pr	OCH_2CF_3
Br	CF_3	C=CHMe
F	SMe	C≡CMe
CN	S(O)Me	NMe_2
OH	$S(O)_2Me$	Ph
Me	OMe	PhO
Et	OEt	4-Me-Ph
i-Pr	OCH_2OMe	4-MeO-Ph
		H

G^2=O, R^{10}=Me

X	Y	R^{11}	R^{12}	R^{28}	R^{31}
CH	N	H	H	H	H
N	CH	H	H	H	H
N	N	H	3-Me	4-Me	H
N	N	H	3-Me	4-Me	6-Me
N	N	Me	H	H	7-Me
N	N	H	H	4-*i*-Pr	6-OMe
N	N	H	3-Me	H	$7-CF_3$
N	N	H	H	4-Et	7-Et
N	N	H	H	4-*i*-Pr	$6-OCHF_2$
N	N	H	H	H	8-Bu
N	N	H	H	4-c-Pr	6-OEt

TABLE 13

Compounds of Formula IIe

G^2=S, R^{12}=H, R^{28}=H

R^{11}		
H	Br	G^2=S, R^{11}=H, R^{28}=H
Me	CF_3	R^{12}
Et	OMe	3-Me
i-Pr	OEt	3-Et
s-Bu	$OCHF_2$	3-*i*-Pr
F	OBu	3-*s*-Bu
Cl	$O(CH_2)_3CF_3$	3-F
	$(CH_2)_3CF_3$	3-Cl
		3-Br

3-CF_3
3-OMe
3-OEt
3-$OCHF_2$
3-OBu
3-$O(CH_2)_3CF_3$
3-$(CH_2)_3CF_3$

G^2=S, R^{11}=R^{12}=H

R^{28}

4-Me
4-CN
4-NO_2
4-OH
4-CO_2H
4-CO_2Et
4-Et
4-*i*-Pr
4-*n*-Hex
4-*c*-Pr
4-CF_3
4-SMe
4-SBu
4-*c*-Hex
4-Cl
4-Br
4-F
4-$(CH_2)_3CF_3$
4-S(O)Me
4-S(O)Bu
4-$S(O)_2Me$
4-$S(O)_2Bu$
4-OMe
4-OBu
4-OCH_2CF_3
4-OCH_2OMe
4-CH_2OMe
4-CH=CH-Me
4-$CH=CHCH_2Me$
4-TBS
4-$SiMe_3$
4-C≡CH
4-C≡C-Et
4-OCH_2C≡CH
4-NMe_2
4-$C(=O)NMe_2$
4-Ph
4-OPh
4-SPh
4-(3-Me-Ph)

G^2=S

R^{11}	R^{12}	R^{28}
Cl	H	6-Cl
H	3-Me	4-Me
H	3-Me	4-Et
H	3-OMe	4-OMe
Me	H	5-Me
Me	H	4-Me
Me	4-Me	5-Me
H	3-Cl	5-Cl
Cl	H	4-Cl

G^2=O, R^{12}=H, R^{28}=H

R^{11}

H
Me
Et
i-Pr
s-Bu
F
Cl
Br
CF_3
OMe
OEt
$OCHF_2$
OBu
$O(CH_2)_3CF_3$
$(CH_2)_3CF_3$

G^2=O, R^{11}=H, R^{28}=H

R^{12}

3-Me
3-Et
3-*i*-Pr
3-*s*-Bu
3-F
3-Cl
3-Br
3-CF_3
3-OMe
3-OEt
3-$OCHF_2$
3-OBu
3-$O(CH_2)_3CF_3$
3-$(CH_2)_3CF_3$
4-Me

G^2=O, R^{11}=R^{12}=H

R^{28}

4-CN
4-NO_2
4-OH
4-CO_2H

4-CO_2Et
4-Et
4-*i*-Pr
4-*n*-Hex
4-*c*-Pr
4-CF_3
4-SMe
4-SBu
4-*c*-Hex
4-Cl
4-Br
4-F
4-$(CH_2)_3CF_3$
4-S(O)Me
4-S(O)Bu
4-$S(O)_2Me$
4-$S(O)_2Bu$
4-OMe
4-OBu
4-OCH_2CF_3
4-OCH_2OMe
4-CH_2OMe
4-CH=CH-Me
4-$CH=CHCH_2Me$
4-TBS
4-$SiMe_3$
4-C≡CH
4-C≡C-Et
4-$OCH_2C≡CH$
4-NMe_2
4-C(=O)NMe_2
4-Ph
4-OPh
4-SPh
4-(3-Me-Ph)

G^2=O

R^{11}	R^{12}	R^{28}
Cl	H	6-Cl
H	3-Me	4-Me
H	3-Me	4-Et
H	3-OMe	4-OMe
Me	H	5-Me
Me	H	4-Me
Me	4-Me	5-Me
H	3-Cl	5-Cl
Cl	H	4-Cl

G^2=S(O), R^{12}=H, R^{28}=H

R^{11}
H
Me
Et
i-Pr
s-Bu
F
Cl
Br
CF_3
OMe
OEt
$OCHF_2$
OBu
$O(CH_2)_3CF_3$
$(CH_2)_3CF_3$

G^2=S(O), R^{11}=H, R^{28}=H

R^{12}
3-Me
3-Et
3-*i*-Pr
3-*s*-Bu
3-F
3-Cl
3-Br
3-CF_3
3-OMe
3-OEt
3-$OCHF_2$
3-OBu
3-$O(CH_2)_3CF_3$
3-$(CH_2)_3CF_3$

G^2=S(O), R^{11}=R^{12}=H

R^{28}
4-Me
4-CN
4-NO_2
4-OH
4-CO_2H
4-CO_2Et
4-Et
4-*i*-Pr
4-*n*-Hex
4-*c*-Pr
4-CF_3
4-SMe
4-SBu
4-*c*-Hex
4-Cl

4-Br
4-F
4-$(CH_2)_3CF_3$
4-S(O)Me
4-S(O)Bu
4-$S(O)_2Me$
4-$S(O)_2Bu$
4-OMe
4-OBu
4-OCH_2CF_3
4-OCH_2OMe
4-CH_2OMe
4-CH=CH-Me
4-$CH=CHCH_2Me$
4-TBS
4-$SiMe_3$
4-C≡CH
4-C≡C-Et
4-$OCH_2C≡CH$
4-NMe_2
4-$C(=O)NMe_2$
4-Ph
4-OPh
4-SPh
4-(3-Me-Ph)

G^2=S(O)

R^{11}	R^{12}	R^{28}
Cl	H	6-Cl
H	3-Me	4-Me
H	3-Me	4-Et
H	3-OMe	4-OMe
Me	H	5-Me
Me	H	4-Me
Me	4-Me	5-Me
H	3-Cl	5-Cl
Cl	H	4-Cl

G^2=$S(O)_2$, R^{12}=H, R^{28}=H

R^{11}
H
Me
Et
i-Pr
s-Bu
F
Cl
Br
CF_3
OMe
OEt
$OCHF_2$
OBu
$O(CH_2)_3CF_3$
$(CH_2)_3CF_3$

G^2=$S(O)_2$, R^{11}=H, R^{28}=H

R^{12}
3-Me
3-Et
3-*i*-Pr
3-*s*-Bu
3-F
3-Cl
3-Br
3-CF_3
3-OMe
3-OEt
3-$OCHF_2$
3-OBu
3-$O(CH_2)_3CF_3$
3-$(CH_2)_3CF_3$

G^2=$S(O)_2$, R^{11}=R^{12}=H

R^{28}
4-Me
4-CN
4-NO_2
4-OH
4-CO_2H
4-CO_2Et
4-Et
4-*i*-Pr
4-*n*-Hex
4-*c*-Pr
4-CF_3
4-SMe
4-SBu
4-*c*-Hex
4-Cl
4-Br
4-F
4-$(CH_2)_3CF_3$
4-S(O)Me
4-S(O)Bu
4-$S(O)_2Me$
4-$S(O)_2Bu$
4-OMe
4-OBu
4-OCH_2CF_3
4-OCH_2OMe
4-CH_2OMe

4-CH=CH-Me
4-CH=CHCH$_2$Me
4-TBS
4-SiMe$_3$
4-C≡CH
4-C≡C-Et
4-OCH$_2$C≡CH
4-NMe$_2$
4-C(=O)NMe$_2$
4-Ph
4-OPh
4-SPh
4-(3-Me-Ph)

G^2=S(O)$_2$

R^{11}	R^{12}	R^{28}
Cl	H	6-Cl
H	3-Me	4-Me
H	3-Me	4-Et
H	3-OMe	4-OMe
Me	H	5-Me
Me	H	4-Me
Me	4-Me	5-Me
H	3-Cl	5-Cl
Cl	H	4-Cl

TABLE 14

Compounds of Formula IIf

n^1=1

R^{27}

H
Et
Bu
i-Pr
CHF$_2$
(CH$_2$)$_3$CF$_3$
CO$_2$Et
C(=O)Me
C(=O)(CH$_2$)$_3$Me
C(=O)Ph
(3-Me-Ph)C(=O)
(4-OMe-Ph)C(=O)
CH$_2$C=CH$_2$
CH$_2$C≡CH
PhCH$_2$
4-Me-PhCH$_2$
S(O)$_2$Me
C(=O)NMe$_2$
C(=S)NHMe
S(O)Me
S(O)$_2$Ph
(4-Me-Ph)S(O)$_2$
C(=O)NHPh
C(=S)NHPh
P(=S)(OEt)$_2$
P(=O)(OEt)$_2$
S(O)$_2$N(Et)$_2$

n^1=2

R^{27}

H
Et
Bu
i-Pr
CHF$_2$
(CH$_2$)$_3$CF$_3$
CO$_2$Et
C(=O)Me
C(=O)(CH$_2$)$_3$Me
C(=O)Ph
(3-Me-Ph)C(=O)
(4-OMe-Ph)C(=O)
CH$_2$C=CH$_2$
CH$_2$C≡CH
PhCH$_2$
4-Me-PhCH$_2$
S(O)$_2$Me
C(=O)NMe$_2$
C(=S)NHMe
S(O)Me
S(O)$_2$Ph
(4-Me-Ph)S(O)$_2$
C(=O)NHPh
C(=S)NHPh
P(=S)(OEt)$_2$
P(=O)(OEt)$_2$
S(O)$_2$N(Et)$_2$

n^1=3

R^{27}

H
Et
Bu
i-Pr
CHF$_2$
(CH$_2$)$_3$CF$_3$
CO$_2$Et
C(=O)Me
C(=O)(CH$_2$)$_3$Me
C(=O)Ph
(3-Me-Ph)C(=O)
(3-Me-Ph)C(=O)
CH$_2$C=CH$_2$
CH$_2$C≡CH

$PhCH_2$
4-Me-$PhCH_2$
$S(O)_2Me$
$C(=O)NMe_2$
$C(=S)NHMe$
$S(O)Me$
$S(O)_2Ph$
(4-Me-Ph)$S(O)_2$
$C(=O)NHPh$
$C(=S)NHPh$
$P(=S)(OEt)_2$
$P(=O)(OEt)_2$
$S(O)_2N(Et)_2$

TABLE 15

Compounds of Formula IIg

n	n^1	G^2		
1	1	S	1	1	S(O)
1	2	S	1	2	S(O)
2	1	S	2	1	S(O)
0	3	S	0	3	S(O)
1	1	O	1	1	$S(O)_2$
1	2	O	1	2	$S(O)_2$
2	1	O	2	1	$S(O)_2$
0	3	O	0	3	$S(O)_2$
			1	1	N-Me
			1	2	N-Me
			2	1	N-Me

TABLE 16

Compounds of Formula IIh

G^2=S

n^2	R^1	R^7	R^4	R^8
1	Me	H	H	H
1	Bu	H	H	H
1	Me	Me	H	H
1	H	H	Me	H
1	H	H	Bu	H
1	Ph	H	H	H
1	4-Me-Ph	H	H	H
1	4-OMe-Ph	H	H	H
0	Me	H	—	—
0	Bu	H	—	—
0	Me	Me	—	—
0	Ph	H	—	—
0	4-Me-Ph	H	—	—

G^2=O

n^2	R^1	R^7	R^4	R^8
1	Me	H	H	H
1	Bu	H	H	H
1	Me	Me	H	H
1	H	H	Me	H
1	H	H	Bu	H
1	Ph	H	H	H
1	4-Me-Ph	H	H	H
1	4-OMe-Ph	H	H	H
0	Me	H	—	—
0	Bu	H	—	—
0	Me	Me	—	—
0	Ph	H	—	—
0	4-Me-Ph	H	—	—

TABLE 17

Compounds of Formula IIi

G^2=S

n^2	R^1	R^2	R^3
0	Me	H	—
0	Bu	H	—
0	H	Me	—
0	H	Bu	—
0	Ph	H	—
0	4-Me-Ph	H	—

0	H	4-OMe-Ph	--
n	R^1	R^2	R^3
1	Me	H	H
1	Bu	H	H
1	H	Me	H
1	H	Bu	H
1	H	H	Me
1	H	H	Bu
1	Ph	H	H
1	4-Me-Ph	H	H
1	H	Ph	H
1	H	4-Me-Ph	H
1	H	H	Ph
1	H	H	4-Me-Ph

G^2=O

n^2	R^1	R^2	R^3
0	Me	H	--
0	Bu	H	--
0	H	Me	--
0	H	Bu	--
0	Ph	H	--
0	4-Me-Ph	H	--
0	H	4-OMe-Ph	--
1	Me	H	H
1	Bu	H	H
1	H	Me	H
1	H	Bu	H
1	H	H	Me
1	H	H	Bu
1	Ph	H	H
1	4-Me-Ph	H	H
1	H	Ph	H
1	H	4-Me-Ph	H
1	H	H	Ph
1	H	H	4-Me-Ph

TABLE 18

Compounds of Formula IIj

G^2=S

R^1	R^7	R^5	R^6
H	H	Me	H
H	H	Ph	H
H	H	H	Me
H	H	H	Ph
Me	H	H	H
Me	Me	H	H
Ph	H	H	H
H	Ph	H	H
H	H	Bu	H
H	H	4-Me-Ph	H
H	H	H	Bu
H	H	H	4-OMe-Ph
Bu	H	H	H
3-Me-Ph	H	H	H
4-OMe-Ph	H	H	H

G^2=O

R^1	R^7	R^5	R^6
H	H	Me	H
H	H	Ph	H
H	H	H	Me
H	H	H	Ph
Me	H	H	H
Me	Me	H	H
Ph	H	H	H

H	Ph	H	H
H	H	Bu	H
H	H	4-Me-Ph	H
H	H	H	Bu
H	H	H	4-OMe-Ph
Bu	H	H	H
3-Me-Ph	H	H	H
4-OMe-Ph	H	H	H

TABLE 19

Compounds of Formula IVc

G^2	n	n^1
S	1	1
S	1	2
S	2	1
O	1	1
O	1	2
O	2	1
S(O)	1	1
S(O)	1	2
S(O)	2	1
$S(O)_2$	1	1
$S(O)_2$	1	2
$S(O)_2$	2	1
NMe	1	1
NMe	1	2
NMe	2	1

TABLE 20

Compounds of Formula Im

G_2=S, MCl_x=$ZnCl_2$

R^{11}	R^{12}	R^{28}
H	Me	H
H	Et	H
H	OMe	H
H	i-Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

G_2=O, MCl_x=$ZnCl_2$

R^{11}	R^{12}	R^{28}
H	Me	H
H	Et	H
H	OMe	H
H	i-Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

G_2=S, MCl_x=$FeCl_3$

R^{11}	R^{12}	R^{28}
H	Me	H
H	Et	H
H	OMe	H
H	i-Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

G_2=O, MCl_x=$FeCl_3$

R^{11}	R^{12}	R^{28}
H	Me	H
H	Et	H
H	OMe	H
H	*i*-Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

G_2=S, MCl_x=$CuCl_2$

R^{11}	R^{12}	R^{28}
H	Me	H
H	Et	H
H	OMe	H
H	*i*-Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

G_2=O, MCl_x=$CuCl_2$

R^{11}	R^{12}	R^{28}
H	Me	H
H	Et	H
H	OMe	H
H	*i*-Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

G_2=S, MCl_x=$MnCl_2$

R^{11}	R^{12}	R^{28}
H	Me	H
H	Et	H
H	OMe	H
H	*i*-Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

G_2=O, MCl_x=$MnCl_2$

R^{11}	R^{12}	R^{28}
H	Me	H
H	Et	H
H	OMe	H
H	*i*-Pr	H
2-Cl	H	H
3-Cl	H	H
H	Cl	H
3-Me	Me	H
2-Me	H	5-Me
2-Cl	H	6-Cl

G_2=S, MCl_x=$MgCl_2$

R^{11}	R^{12}	R^{28}
H	Me	H
H	Et	H
H	OMe	H

H	i-Pr	H	H	Et	H
2-Cl	H	H	H	OMe	H
3-Cl	H	H	H	i-Pr	H
H	Cl	H	2-Cl	H	H
3-Me	Me	H	3-Cl	H	H
2-Me	H	5-Me	H	Cl	H
2-Cl	H	6-Cl	3-Me	Me	H
			2-Me	H	5-Me
G_2=O, MCl_x=$MgCl_2$			2-Cl	H	6-Cl
R^{11}	R^{12}	R^{28}			
H	Me	H			

Formulation/Utility

Compounds of this invention will generally be used in formulation with an agriculturally suitable composition. The fungicidal compositions of the present invention comprise an effective amount of at least one compound of Formula I as defined above and at least one of (a) a surfactant, (b) an organic solvent, and (c) at least one solid or liquid diluent. Useful formulations can be prepared in conventional ways. They include dusts, granules, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates, dry flowables and the like. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The formulations will typically contain effective amounts of active ingredient, diluent and surfactant within the following approximate ranges which add up 100 weight percent.

	Weight Percent		
	Active Ingredient	Diluent	Surfactant
Wettable Powders	25-90	0-74	1-10
Oil Suspensions, Emulsions, Solutions, (including Emulsifiable Concentrates)	5-50	40-95	0-15
Dusts	1-25	70-99	0-5
Granules, Baits and Pellets	0.01-99	5-99.99	0-15
High Strength Compositions	90-99	0-10	0-2

Typical solid diluents are described in Watkins, et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey. Typical liquid diluents and solvents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950. *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth, etc.

Methods for formulating such compositions are well known. Solutions are prepared by simply mixing the ingredients. Fine solid compositions are made by blending and, usually, grinding as in a hammer mill or fluid energy mill. Water-dispersible granules can be produced be agglomerating a fine powder composition; see for example, Cross et al., *Pesticide Formulations*, Washington, D.C., 1988, pp 251-259. Suspensions are prepared by wet-milling; see, for example, U.S. 3,060,084. Granules and pellets can be made by

spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147-148, *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, New York, 1963, pp 8-57 and following, and WO 91/13546. Pellets can be prepared as described in U.S. 4,172,714. Water-dispersible and water-soluble granules can be prepared as taught in DE 3,246,493.

For further information regarding the art of formulation, see U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10 through 41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138-140, 162-164, 166, 167 and 169-182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, 1961, pp 81-96; and Hance et al., *Weed Control Handbook*, 8th Ed., Blackwell Scientific Publications, Oxford, 1989.

In the following Examples, all percentages are by weight and all formulations are worked up in conventional ways. Compound numbers refer to Index Table A hereinafter.

Example A

Wettable Powder

Compound 11	65.0%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
sodium silicoaluminate	6.0%
montmorillonite (calcined)	23.0%.

Example B

Granule

Compound 11	10.0%
attapulgite granules (low volative	

matter, 0.71/0.30 mm; U.S.S. No. 25-50 sieves)	90.0%.

Example C

Extruded Pellet

Compound 11	25.0%
anhydrous sodium sulfate	10.0%
crude calcium ligninsulfonate	5.0%
sodium alkylnaphthalenesulfonate	1.0%
calcium/magnesium bentonite	59.0%.

Example D

Emulsifiable Concentrate

Compound 11	20.0%
blend of oil soluble sulfonates and polyoxyethylene ethers	10.0%
isophorone	70.0%.

The compounds of this invention are useful as plant disease control agents. The present invention therefore further comprises a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a compound of Formula I or a fungicidal composition containing said compound. The compounds and compositions of this invention provide control of diseases caused by a broad spectrum of fungal plant pathogens in the *Basidiomycete, Ascomycete, Oomycete* and *Deuteromycete* classes. They are effective in controlling a broad spectrum of plant diseases, particularly foliar pathogens of ornamental, vegetable, field, cereal, and fruit crops. These pathogens include *Plasmopara viticola, Phytophthora infestans, Peronospora tabacina, Pseudoperonospora cubensis, Pythium aphanidermatum, Alternaria brassicae, Septoria nodorum, Cercosporidium personatum, Cercospora arachidicola, Pseudocercosporella herpotrichoides,*

Cercospora beticola, Botrytis cinerea, Monilinia fructicola, Pyricularia oryzae, Podosphaera leucotricha, Venturia inaequalis, Erysiphe graminis, Uncinula necatur, Puccinia recondita, Puccinia graminis, Hemileia vastatrix, Puccinia striiformis, Puccinia arachidis, Rhizoctonia solani, Sphaerotheca fuliginea, Fusarium oxysporum, Verticillium dahliae, Pythium aphanidermatum, Phytophthora megasperma and other genera and species closely related to these pathogens.

Compounds of this invention can also be mixed with one or more other insecticides, fungicides, nematocides, bactericides, acaricides, semiochemicals, repellants, attractants, pheromones, feeding stimulants or other biologically active compounds to form a multi-component pesticide giving an even broader spectrum of agricultural protection. Examples of other agricultural protectants with which compounds of this invention can be formulated are: insecticides such as monocrotophos, carbofuran, tetrachlorvinphos, malathion, parathion-methyl, methomyl, chlordimeform, diazinon, deltamethrin, oxamyl, fenvalerate, esfenvalerate, permethrin, profenofos, sulprofos, triflumuron, diflubenzuron, methoprene, buprofezin, thiodicarb, acephate, azinphosmethyl, chlorpyrifos, dimethoate, fipronil, flufenprox, fonophos, isofenphos, methidathion, methamidophos, phosmet, phosphamidon, phosalone, pirimicarb, phorate, terbufos, trichlorfon, methoxychlor, bifenthrin, biphenate, cyfluthrin, fenpropathrin, fluvalinate, flucythrinate, tralomethrin, metaldehyde and rotenone; fungicides such as carbendazim, thiuram, dodine, maneb, chloroneb, benomyl, cymoxanil, fenpropidine, fenpropimorph, triadimefon, captan, thiophanate-methyl, thiabendazole, phosethyl-Al, chlorothalonil, dichloran, metalaxyl,

captafol, iprodione, oxadixyl, vinclozolin, kasugamycin, myclobutanil, tebuconazole, difenoconazole, diniconazole, fluquinconazole, ipconazole, metconazole, penconazole, propiconazole, uniconzole, flutriafol, prochloraz, pyrifenox, fenarimol, triadimenol, diclobutrazol, copper oxychloride, furalaxyl, folpet, flusilazol, blasticidin S, diclomezine, edifenphos, isoprothiolane, iprobenfos, mepronil, neo-asozin, pencycuron, probenazole, pyroquilon, tricyclazole, validamycin, and flutolanil; nematocides such as aldoxycarb, fenamiphos and fosthietan; bactericides such as oxytetracyline, streptomycin and tribasic copper sulfate; acaricides such as binapacryl, oxythioquinox, chlorobenzilate, dicofol, dienochlor, cyhexatin, hexythiazox, amitraz, propargite, tebufenpyrad and fenbutatin oxide; and biological agents such as Bacillus thuringiensis, baculovirus and avermectin B.

In certain instances, combinations with other fungicides having a similiar spectrum of control but a different mode of action will be particularly advantageous for resistance management.

Plant disease control is ordinarily accomplished by applying an effective amount of a compound of this invention either pre- or post-infection, to the portion of the plant to be protected such as the roots, stems, foliage, fruit, seeds, tubers or bulbs, or to the media (soil or sand) in which the plants to be protected are growing. The compounds can also be applied to the seed to protect the seed and seedling.

Rates of application for these compounds can be influenced by many factors of the environment and should be determined under actual use conditions. Foliage can normally be protected when treated at a rate of from less than 1 g/ha to 5,000 g/ha of active

ingredient. Seed and seedlings can normally be protected when seed is treated at a rate of from 0.1 to 10 g per kilogram of seed.

The following Tests demonstrate the control efficacy of compounds of this invention on specific pathogens. The pathogen control protection afforded by the compounds is not limited, however, to these species. See Index Table A for compound descriptions.

Test compounds were first dissolved in acetone in an amount equal to 3% of the final volume and then suspended at a concentration of 200 ppm in purified water containing 250 ppm of the surfactant Trem® 014 (polyhydric alcohol esters). The resulting test suspensions were then used in the following tests.

TEST A

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore dust of *Erysiphe graminis f. sp. tritici*, (the causal agent of wheat powdery mildew) and incubated in a growth chamber at 20°C for 7 days, after which disease ratings were made.

TEST B

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Puccinia recondita* (the causal agent of wheat leaf rust) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth chamber at 20°C for 6 days, after which disease ratings were made.

TEST C

The test suspension was sprayed to the point of run-off on rice seedlings. The following day the seedlings were inoculated with a spore suspension of *Pyricularia oryzae* (the causal agent of rice blast) and incubated in a saturated atmosphere at 27°C for 24 h,

and then moved to a growth chamber at 30°C for 5 days, after which disease ratings were made.

TEST D

The test suspension was sprayed to the point of run-off on tomato seedlings. The following day the seedlings were inoculated with a spore suspension of *Phytophthora infestans* (the causal agent of potato and tomato late blight) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth chamber at 20°C for 5 days, after which disease ratings were made.

TEST E

The test suspension was sprayed to the point of run-off on grape seedlings. The following day the seedlings were inoculated with a spore suspension of *Plasmopara viticola* (the causal agent of grape downy mildew) and incubated in a saturated atmosphere at 20°C for 24 h, moved to a growth chamber at 20°C for 6 days, and then incubated in a saturated atmosphere at 20°C for 24 h, after which disease ratings were made.

TEST F

The test suspension was sprayed to the point of run-off on cucumber seedlings. The following day the seedlings were inoculated with a spore suspension of *Botrytis cinerea* (the causal agent of gray mold on many crops) and incubated in a saturated atmosphere at 20°C for 48 h, and moved to a growth chamber at 20°C for 5 days, after which disease ratings were made.

Index Table 1

Compounds of Formula I

R^9=R^{10}=Me; X=CH; Y=N

Cmpd. No.	G^1-G^2-G^3	E	mp (°C)
1	CH_2OCH_2	Ph	a
2	CH_2CH_2S	4-Cl-Ph	a

3	CH_2OCH_2	4-Et-Ph	a
4	CH_2CH_2O	3-Me-Ph	a
5	CH_2CH_2S	3-Me-Ph	a
6	CH_2CH_2O	2,6-diCl-Ph	a
7	CH_2CH_2S	4-Me-Ph	a
8	CH_2CH_2S	2-Cl-Ph	146-148
9	CH_2CH_2S	3-Cl-Ph	a
10	CH_2CH_2O	4-Et-Ph	99-106
11	CH_2CH_2S	4-Et-Ph	84-87
12	CH_2CH_2SO	2-Cl-Ph	168-170
13	CH_2CH_2S	Ph	142-145
14	CH_2CH_2S	3-CF_3-Ph	105-110
15	CH_2CH_2S	4-OMe-Ph	111-115
16	CH_2CH_2SO	4-Et-Ph	149-164
17	$CH_2CH_2SO_2$	4-Et-Ph	139-141
18	CH_2CH_2S	4-t-Bu	114-121
19	$CH_2CH_2CH_2S$	4-OMe-Ph	119-123
20	CH_2CH_2S	OPh	75-85
21	$CH_2CH_2CH_2S$	4-Et-Ph	97-100
22	$CH(CH_3)CH_2S$	4-Et-Ph	a
23	CH_2CH_2S	2-Me-Ph	86-91
24	CH_2CH_2S	OBzl	81-93
25	CH_2CH_2S	SPh	a
26	CH_2CH_2S	Bzl	a
27	$CH_2CH_2CH_2S$	Ph	158-160
28	$CH(CH_3)CH_2S$	Ph	a
29	$CH_2C(CH_3)_2CH_2S$	Ph	116-121
30	$CH_2CH(Ph)S$	Ph	196-208
31	CH_2CH_2S	Et	a
32	$CH_2CH(CO_2Et)S$	Ph	124-133
33	$CH_2CH(Ph)SO_2$	Ph	201-206
34	$CH(CF_3)CH_2S$	Ph	174-181
35	$CH(CH_2CH_3)CH_2S$	Ph	a
36	$CH_2CH(CN)S$	Ph	208-212
37	$CH(CN)CH_2S$	Ph	168-174

38	CH_2CH_2S	3,4-diCl-Ph	149-152
39	CH_2CH_2S	4-Ph-Ph	151-155
40	CH_2CH_2S	3,4-diOMe-Ph	172-174

[a] Oil or gum; ^1H NMR data in Index Table 2.

X=CR^{13}; R^9 and R^{13} are taken together to form a fused benzene ring; Y=N; R^{10}=Me

Cmpd. No.	G^1-G^2-G^3	E	mp (°C)
38	CH_2CH_2S	Ph	102-108

R^9=R^{10}=ethyl; X=CH; Y=N

Cmpd. No.	G^1-G^2-G^3	E	mp (°C)
39	CH_2CH_2S	Ph	oil; ^1H NMR data in Index Table 2.

Index Table 2

Cmpd. No.	^1H NMR Data[a]
1	7.75 (m, 2H), 7.37 (m, 3H), 6.57 (s, 1H), 5.54 (s, 2H), 4.83 (s, 2H), 2.42 (s, 6H).
2	7.83 (d, 2H), 7.35 (d, 2H), 6.56 (s, 1H), 4.47 (t, 2H), 3.36 (t, 2H), 2.43 (s, 6H).
3	7.66 (d, 2H), 7.21 (d, 2H), 6.56 (s, 1H), 5.54 (s, 2H), 4.81 (s, 2H), 2.67 (q, 2H), 2.42 (s, 6H), 1.24 (t, 3H).
4	7.82 (m, 1H), 7.75 (m, 1H), 7.25 (m, 1H), 7.19 (m, 1H), 6.49 (s, 1H), 4.54 (m, 2H), 4.28 (m, 2H), 2.42 (s, 6H), 2.38 (s, 3H).
5	7.7 (m, 2H), 7.2 (m, 2H), 6.54 (s, 1H), 4.45 (m, 2H), 3.35 (m, 2H), 2.42 (s, 6H), 2.39 (s, 3H).
6	7.31 (m, 2H), 7.25 (m, 1H), 6.5 (s, 1H), 4.55 (m, 2H), 4.35 (m, 2H), 2.38 (s, 6H).

7	7.77 (d, 2H), 7.18 (d, 2H), 6.53 (s, 1H), 4.46 (m, 2H), 3.35 (m, 2H), 2.42 (s, 6H), 2.37 (s, 3H).
9	7.90 (m, 1H), 7.75 (m, 1H), 7.3 (m, 2H), 6.57 (s, 1H), 4.47 (m, 2H), 3.36 (m, 2H), 2.43 (s, 6H).
22	7.82 (d, 2H), 7.22 (d, 2H), 6.52 (s, 1H), 5.7 (m, 1H), 3.45 (d, 1H), 3.00 (d, 1H), 2.7 (q, 2H), 2.42 (s, 6H), 1.38 (d, 3H), 1.24 (t, 3H).
25	7.65 (m, 2H), 7.34 (m, 3H), 6.55 (s, 1H), 4.40 (m, 2H), 3.25 (m, 2H), 2.41 (s, 6H).
26	7.37 (d, 2H), 7.32 (t, 2H), 7.25 (d, 1H), 6.51 (s, 1H), 4.32 (m, 2H), 3.89 (s, 2H), 3.19 (m, 2H), 2.41 (s, 6H).
28	7.93 (d, 2H), 7.37 (m, 3H), 6.54 (s, 1H), 5.7 (m, 1H), 3.45 (d, 1H), 3.02 (m, 1H), 2.42 (s, 6H), 1.40 (d, 3H).
31	6.48 (s, 1H), 4.33 (t, 2H), 3.25 (t, 2H), 2.58 (q, 2H), 2.39 (s, 6H), 1.26 (t, 3H).
35	7.85 (d, 2H), 7.37 (m, 3H), 6.52 (s, 1H), 5.50 (m, 1H), 3.38 (d, 1H), 3.20 (d, 1H), 2.41 (s, 6H), 1.80 (m, 2H), 0.99 (t, 3H).
39	7.85 (d, 2H), 7.37 (m, 3H), 6.56 (s, 1H), 4.45 (m, 2H), 3.35 (m, 2H), 2.72 (q, 4H), 1.31 (t, 6H).

[a] ^1H NMR data are in ppm downfield from tetramethylsilane. Coupling are designated (s)-singlet, (d)-doublet, (t)-triplet, (q)-quartet, (m)-multiplet. Samples were dissolved in $CDCl_3$.

Results for Tests A-F are given in Table A. In the table, a rating of 100 indicates 100% disease control and a rating of 0 indicates no disease control (relative to the controls). NT = Not Tested.

Table A

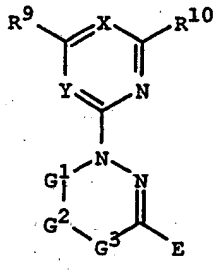
Cmpd No.	Test A	Test B	Test C	Test D	Test E	Test F
1	98	100	65	23	75	65
2	76	93	99	11	91	2
3	86*	84*	72*	59*	44	77
4	73*	64*	73*	36*	0*	32*
5	24*	64*	73*	10*	0*	32*
6	0*	0*	29*	0*	86*	46*
8	0	80	85	3	100	98
9	98	100	99	82	92	98
10	94	100	99	52	85	82
11	99	100	97	52	92	98
12	56	0	0	60	92	0
13	98	96	91	91	100	77
14	98	82	100	73	100	47
15	96	98	97	0	100	98
16	82	0	0	0	13	0
17	61	14	0	NT	14	0
18	82	0	86	0	73	83
19	29	21	57	18	96	99
20	90	98	99	85	99	99
21	98	98	94	0	100	69
22	0	55	91	58	100	0
23	74	100	94	73	100	80
24	83	91	32	63	84	0
25	90	100	91	63	100	70
26	92	98	85	70	100	46
27	55	23	91	14	74	98
28	56*	96	91	0	100	94
29	52	80	74	22*	92	94
30	0	55	0	22	99	66
31	89	55	0	44	0	66
32	0	0	0	0	99	82
33	0*	54*	0*	0*	9*	34*
34	0*	54*	0*	0*	0*	0*

38	29	93	97	23	96	0
39	98	83	91	0	100	90

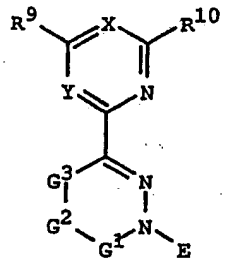
*=Applications of the compound was made at a rate of 40 ppm.

What is claimed is:

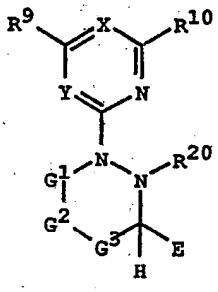
1. The compounds of Formulae I, II, III and IV,



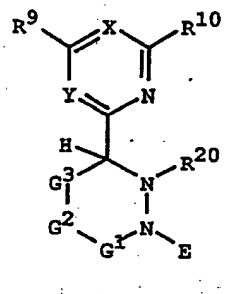
I



II



III



IV

wherein:

$-G^1-G^2-G^3-$ taken together with the attached atoms form a 5-8 membered ring, wherein

$-G^1-$ is $-CR^1R^7-$; $-(CHR^1CHR^2)-$; $-(CHR^1CHR^2CHR^3)-$; or $-(CHR^1CHR^2CHR^3CHR^4)-$;

$-G^2-$is $-O-$; $-S-$; $-S(O)-$; $-S(O)_2-$ or $-NR^{27}-$;

$-G^3-$is $-CR^4R^8-$; $-(CHR^5CHR^6)-$; $-(CHR^3CHR^5CHR^6)-$ or a direct bond;

X is N or CR^{13};

Y is N or CR^{14};

E is H; C_1-C_6 alkyl; C_3-C_7 cycloalkyl optionally substituted with 1-2 methyl; C_1-C_6 haloalkyl; C_1-C_6 alkylthio; C_1-C_6 alkoxy; C_1-C_6 haloalkoxy; or phenyl, phenoxy, phenylthio, phenylamino,

phenylmethyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, 2-naphthalenyl, thienyl, furanyl or pyridyl each optionally substituted with R^{11}, R^{12} and R^{28};

R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are each independently H; C_1-C_4 alkyl; C_1-C_4 haloalkyl, halogen, CO_2CH_3, $CO_2CH_2CH_3$, cyano or phenyl optionally substituted with R^{25};

provided that

(i) the maximum number of carbon atoms in $-G^1-G^2-G^3-$ with geminal disubstitution is one;

(ii) the maximum number of optionally substituted phenyl substituents on $-G^1-G^2-G^3-$ is one;

(iii) $-G^3-$ is other than a direct bond in compounds of Formulae III and IV; and

(iv) $-G^2-G^3-$ is other than $-NR^{27}-$ in compounds of Formulae I and II;

R^9, R^{10} and R^{13} are each independently H; halogen; cyano; hydroxy; C_1-C_6 alkyl; C_1-C_4 haloalkyl; C_1-C_4 alkylthio; C_1-C_4 alkylsulfinyl; C_1-C_4 alkylsulfonyl; C_3-C_6 cycloalkyl optionally substituted with 1-2 methyl groups; C_1-C_4 alkoxy; C_1-C_4 haloalkoxy; C_2-C_4 alkoxyalkyl; C_2-C_4 alkenyl; C_2-C_4 haloalkenyl; C_2-C_4 alkenyloxy; C_2-C_4 alkynyl; C_2-C_4 alkynyloxy; $NR^{29}R^{30}$; or phenyl or phenoxy optionally substituted with R^{31}; or

R^9 and R^{13}, or R^{10} and R^{13}, or R^9 and R^{14} can be taken together to form $-(CH_2)_3-$, $-(CH_2)_4-$ or a fused benzene ring optionally substituted with R^{31};

R^{11}, R^{12}, R^{21}, R^{24}, R^{26} and R^{31} are each independently halogen; C_1-C_4 alkyl; C_1-C_4 haloalkyl; C_1-C_4 alkoxy; or C_1-C_4 haloalkoxy;

R^{14} is H; halogen; C_1-C_2 alkyl; or C_1-C_2 alkoxy;

R^{15}, R^{16}, R^{17}, R^{18}, R^{29} and R^{30} are each independently H or C_1-C_2 alkyl; or

R^{15} and R^{16}, or R^{17} and R^{18}, or R^{29} and R^{30} can be taken together along with the nitrogen atom to which they are attached to form a 4-morpholinyl, pyrrolidinyl or piperidinyl ring;

R^{20} and R^{27} are each independently H; C_1-C_4 alkyl; C_1-C_4 haloalkyl; C_2-C_5 alkylcarbonyl; phenylcarbonyl optionally substituted with R^{21}; C_3-C_4 alkenyl; C_3-C_4 alkynyl; phenylmethyl optionally substituted with R^{21} on the phenyl ring; C_1-C_4 alkylsulfinyl; C_1-C_4 alkylsulfonyl; phenylsulfinyl, phenylsulfonyl or phenoxycarbonyl each optionally substituted with R^{21}; C_2-C_4 alkoxycarbonyl; $C(=O)NR^{22}R^{23}$; $C(=S)NHR^{23}$; $P(=S)(C_1$-C_4 alkoxy$)_2$; $P(=O)(C_1$-C_4 alkoxy$)_2$; or $S(=O)_2NR^{22}R^{23}$;

R^{22} is H or C_1-C_3 alkyl;

R^{23} is C_1-C_4 alkyl; or phenyl optionally substituted with R^{24}; or

R^{22} and R^{23} can be taken together along with the nitrogen atom to which they are attached to form a 4-morpholinyl, pyrrolidinyl, piperidinyl or imidazolyl ring;

R^{25} is 1-2 halogen; C_1-C_4 alkyl; C_1-C_4 haloalkyl; C_1-C_4 alkoxy; C_1-C_4 haloalkoxy; nitro; cyano or C_1-C_4 alkylthio; and

R^{28} is halogen; cyano; nitro; hydroxy; hydroxycarbonyl; C_1-C_6 alkyl; C_3-C_6 cycloalkyl; C_1-C_6 haloalkyl; C_1-C_4 alkylthio; C_1-C_4 alkyl-

sulfinyl; C_1-C_4 alkylsulfonyl; (C_1-C_4 alkyl)$_3$silyl; C_2-C_5 alkylcarbonyl; C_2-C_4 alkenyl; C_3-C_4 alkenyloxy; C_2-C_4 alkynyl; C_3-C_4 alkynyloxy; C_1-C_4 alkoxy; C_1-C_4 haloalkoxy; C_2-C_4 alkoxyalkyl; C_2-C_5 alkoxycarbonyl; C_2-C_4 alkoxyalkoxy; $NR^{15}R^{16}$; $C(=O)NR^{17}R^{18}$; or phenyl, phenoxy or phenylthio each optionally substituted with R^{26};

provided that

when E is, C_1-C_6 alkylthio, C_1-C_6 alkoxy, C_1-C_6 haloalkoxy, phenoxy, phenylthio or phenylamino, then E may only substitute compounds of Formula I.

and agriculturally suitable salts and metal complexes thereof.

2. The compounds of Claim 1, Formula I, wherein:

Y is N;

E is phenyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, thienyl, or pyridyl each optionally substituted with R^{11}, R^{12} and R^{28};

R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are each independently H or methyl;

R^{11} and R^{12} are each independently F, Cl, methyl, trifluoromethyl, methoxy or trifluoromethoxy;

R^{13} is H;

R^9 and R^{10} are each independently halogen; C_1-C_4 alkyl; cyclopropyl; C_1-C_4 haloalkyl; allyl; or C_2-C_3 alkynyl; or

R^9 and R^{13} can be taken together to form a fused benzene ring optionally substituted with R^{31};

R^{28} is halogen; cyano; C_1-C_4 alkyl; C_1-C_4 haloalkyl; allyl; propargyl; C_1-C_4 alkoxy;

C_1-C_4 haloalkoxy; or phenyl or phenoxy each optionally substituted with R^{26}; and

R^{31} is halogen; C_1-C_4 alkyl or C_1-C_4 haloalkyl.

3. The compounds of Claim 2, wherein:

G^2 is O; S or NR^{27}; and

E is phenyl optionally substituted with R^{11}, R^{12} and R^{28}; indanyl or tetrahydronaphthalenyl.

4. The compounds of Claim 3, wherein:

G^2 is O; S; NH or N(C_1-C_4 alkyl); and

E is phenyl optionally substituted with R^{11}, R^{12} and R^{28}.

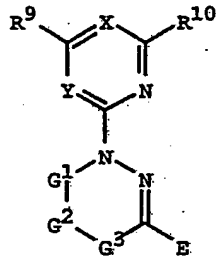
5. The compound of Claim 1, which is 3-(4,6-dimethyl-2-pyrimidinyl)-3,6-dihydro-5-phenyl-2H-1,3,4-oxadiazine.

6. The compound of Claim 1, which is 3-(4,6-dimethyl-2-pyrimidinyl)-5-(4-ethyl-phenyl)-3,6-dihydro-2H-1,3,4-oxadiazine.

7. The compound of Claim 1, which is 2-(2-chlorophenyl)-4-(4,6-dimethyl-2-pyrimidinyl)-5,6-dihydro-4H-1,3,4-thiadiazine.

8. The compound of Claim 1, which is 4-(4,6-dimethyl-2-pyrimidinyl)-2-(4-ethyl-phenyl)-5,6-dihydro-4H-1,3,4-thiadiazine.

9. A method of controlling fungus disease in plants which comprises treating the locus to be protected with an effective amount of at least one of the compounds of Formulae I, II, III or IV, agriculturally suitable salts thereof, agriculturally suitable metal complexes thereof, or agricultural compositions containing them;



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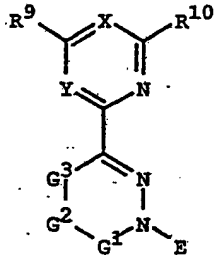

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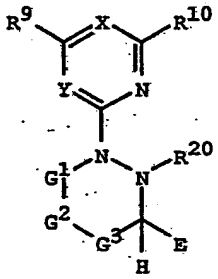

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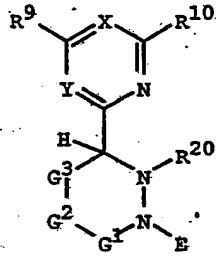


IV

wherein:

$-G^1-G^2-G^3-$ taken together with the attached atoms form a 5-8 membered ring, wherein

$-G^1-$ is $-CR^1R^7-$; $-(CHR^1CHR^2)-$; $-(CHR^1CHR^2CHR^3)-$; or $-(CHR^1CHR^2CHR^3CHR^4)-$;

$-G^2-$ is $-O-$; $-S-$; $-S(O)-$; $-S(O)_2-$ or $-NR^{27}-$;

$-G^3-$ is $-CR^4R^8-$; $-(CHR^5CHR^6)-$; $-(CHR^3CHR^5CHR^6)-$ or a direct bond;

X is N or CR^{13};

Y is N or CR^{14};

E is H; C_1-C_6 alkyl; C_3-C_7 cycloalkyl optionally substituted with 1-2 methyl; C_1-C_6 haloalkyl; C_1-C_6 alkylthio; C_1-C_6 alkoxy; C_1-C_6 haloalkoxy; or phenyl, phenoxy, phenylthio, phenylamino, phenylmethyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, 2-naphthalenyl, thienyl, furanyl or pyridyl each optionally substituted with R^{11}, R^{12} and R^{28};

R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are each independently H; C_1-C_4 alkyl; C_1-C_4 haloalkyl, halogen, CO_2CH_3, $CO_2CH_2CH_3$, cyano, or phenyl optionally substituted with R^{25};

provided that

(i) the maximum number of carbon atoms in $-G^1-G^2-G^3-$ with geminal disubstitution is one;

(ii) the maximum number of optionally substituted phenyl substituents on $-G^1-G^2-G^3-$ is one;

(iii) $-G^3-$ is other than a direct bond in compounds of Formulae III and IV; and

(iv) $-G^2-G^3-$ is other than $-NR^{27}-$ in compounds of Formulae I and II;

R^9, R^{10} and R^{13} are each independently H; halogen; cyano; hydroxy; C_1-C_6 alkyl; C_1-C_4 haloalkyl; C_1-C_4 alkylthio; C_1-C_4 alkylsulfinyl; C_1-C_4 alkylsulfonyl; C_3-C_6 cycloalkyl optionally substituted with 1-2 methyl groups; C_1-C_4 alkoxy; C_1-C_4 haloalkoxy; C_2-C_4 alkoxyalkyl; C_2-C_4 alkenyl; C_2-C_4 haloalkenyl; C_2-C_4 alkenyloxy; C_2-C_4 alkynyl; C_2-C_4 alkynyloxy; $NR^{29}R^{30}$; or phenyl or phenoxy optionally substituted with R^{31}; or

R^9 and R^{13}, or R^{10} and R^{13}, or R^9 and R^{14} can be taken together to form $-(CH_2)_3-$, $-(CH_2)_4-$ or a fused benzene ring optionally substituted with R^{31};

R^{11}, R^{12}, R^{21}, R^{24}, R^{26} and R^{31} are each independently halogen; C_1-C_4 alkyl; C_1-C_4 haloalkyl; C_1-C_4 alkoxy; or C_1-C_4 haloalkoxy;

R^{14} is H; halogen; C_1-C_2 alkyl; or C_1-C_2 alkoxy;

R^{15}, R^{16}, R^{17}, R^{18}, R^{29} and R^{30} are each independently H or C_1-C_2 alkyl; or

R^{15} and R^{16}, or R^{17} and R^{18}, or R^{29} and R^{30} can be taken together along with the nitrogen atom to which they are attached to form a 4-morpholinyl, pyrrolidinyl or piperidinyl ring;

R^{20} and R^{27} are each independently H; C_1-C_4 alkyl; C_1-C_4 haloalkyl; C_2-C_5 alkylcarbonyl; phenylcarbonyl optionally substituted with R^{21}; C_3-C_4 alkenyl; C_3-C_4 alkynyl; phenylmethyl optionally substituted with R^{21} on the phenyl ring; C_1-C_4 alkylsulfinyl; C_1-C_4 alkylsulfonyl; phenylsulfinyl, phenylsulfonyl or phenoxycarbonyl each optionally substituted with R^{21}; C_2-C_4 alkoxycarbonyl; $C(=O)NR^{22}R^{23}$; $C(=S)NHR^{23}$; $P(=S)(C_1$-C_4 alkoxy$)_2$; $P(=O)(C_1$-C_4 alkoxy$)_2$; or $S(=O)_2NR^{22}R^{23}$;

R^{22} is H or C_1-C_3 alkyl;

R^{23} is C_1-C_4 alkyl; or phenyl optionally substituted with R^{24}; or

R^{22} and R^{23} can be taken together along with the nitrogen atom to which they are attached to form a 4-morpholinyl, pyrrolidinyl, piperidinyl or imidazolyl ring;

R^{25} is 1-2 halogen; C_1-C_4 alkyl; C_1-C_4 haloalkyl; C_1-C_4 alkoxy; C_1-C_4 haloalkoxy; nitro; cyano or C_1-C_4 alkylthio; and

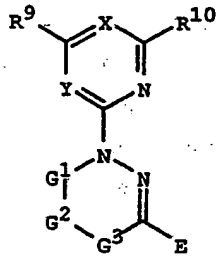
R^{28} is halogen; cyano; nitro; hydroxy; hydroxycarbonyl; C_1-C_6 alkyl; C_3-C_6 cycloalkyl; C_1-C_6 haloalkyl; C_1-C_4 alkylthio; C_1-C_4 alkylsulfinyl; C_1-C_4 alkylsulfonyl; (C_1-C_4 alkyl$)_3$silyl; C_2-C_5 alkylcarbonyl; C_2-C_4 alkenyl; C_3-C_4 alkenyloxy; C_2-C_4 alkynyl; C_3-C_4 alkynyloxy; C_1-C_4 alkoxy; C_1-C_4 haloalkoxy; C_2-C_4 alkoxyalkyl; C_2-C_5 alkoxycarbonyl; C_2-C_4 alkoxyalkoxy; $NR^{15}R^{16}$; $C(=O)NR^{17}R^{18}$; or phenyl,

phenoxy or phenylthio each optionally substituted with R^{26}.

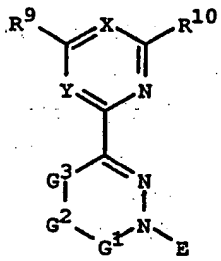
provided that

when E is, C_1-C_6 alkylthio, C_1-C_6 alkoxy, C_1-C_6 haloalkoxy, phenoxy, phenylthio or phenylamino, then E may only substitute compounds of Formula I.

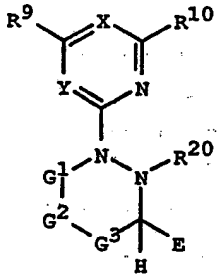
10. A fungicidal composition comprising a fungicidally effective amount of a compound of Formula I, II, III or IV



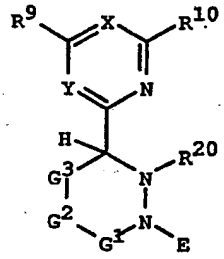
I



II



III



IV

wherein:

$-G^1-G^2-G^3-$ taken together with the attached atoms form a 5-8 membered ring, wherein

$-G^1-$ is $-CR^1R^7-$; $-(CHR^1CHR^2)-$; $-(CHR^1CHR^2CHR^3)-$; or $-CHR^1CHR^2CHR^3CHR^4)-$;

$-G^2-$is $-O-$; $-S-$; $-S(O)-$; $-S(O)_2-$ or $-NR^{27}-$;

$-G^3-$ is $-CR^4R^8-$; $-(CHR^5CHR^6)-$; $-(CHR^3CHR^5CHR^6)-$ or a direct bond;

X is N or CR^{13};

Y is N or CR^{14};

E is H; C_1-C_6 alkyl; C_3-C_7 cycloalkyl optionally substituted with 1-2 methyl; C_1-C_6 haloalkyl; C_1-C_6 alkylthio; C_1-C_6 alkoxy; C_1-C_6 haloalkoxy; or phenyl, phenoxy, phenylthio, phenylamino, phenylmethyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, 2-naphthalenyl, thienyl, furanyl or pyridyl each optionally substituted with R^{11}, R^{12} and R^{28};

R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are each independently H; C_1-C_4 alkyl; C_1-C_4 haloalkyl, halogen, CO_2CH_3, $CO_2CH_2CH_3$, cyano or phenyl optionally substituted with R^{25};

provided that

(i) the maximum number of carbon atoms in $-G^1-G^2-G^3-$ with geminal disubstitution is one;

(ii) the maximum number of optionally substituted phenyl substituents on $-G^1-G^2-G^3-$ is one;

(iii) $-G^3-$ is other than a direct bond in compounds of Formulae III and IV; and

(iv) $-G^2-G^3-$ is other than $-NR^{27}-$ in compounds of Formulae I and II;

R^9, R^{10} and R^{13} are each independently H; halogen; cyano; hydroxy; C_1-C_6 alkyl; C_1-C_4 haloalkyl; C_1-C_4 alkylthio; C_1-C_4 alkylsulfinyl; C_1-C_4 alkylsulfonyl; C_3-C_6 cycloalkyl optionally substituted with 1-2 methyl groups; C_1-C_4 alkoxy; C_1-C_4 haloalkoxy; C_2-C_4 alkoxyalkyl; C_2-C_4 alkenyl; C_2-C_4 haloalkenyl; C_2-C_4 alkenyloxy; C_2-C_4 alkynyl; C_2-C_4 alkynyloxy;

$NR^{29}R^{30}$; or phenyl or phenoxy optionally substituted with R^{31}; or

R^9 and R^{13}, or R^{10} and R^{13}, or R^9 and R^{14} can be taken together to form $-(CH_2)_3-$, $-(CH_2)_4-$ or a fused benzene ring optionally substituted with R^{31};

R^{11}, R^{12}, R^{21}, R^{24}, R^{26} and R^{31} are each independently halogen; C_1-C_4 alkyl; C_1-C_4 haloalkyl; C_1-C_4 alkoxy; or C_1-C_4 haloalkoxy;

R^{14} is H; halogen; C_1-C_2 alkyl; or C_1-C_2 alkoxy;

R^{15}, R^{16}, R^{17}, R^{18}, R^{29} and R^{30} are each independently H or C_1-C_2 alkyl; or

R^{15} and R^{16}, or R^{17} and R^{18}, or R^{29} and R^{30} can be taken together along with the nitrogen atom to which they are attached to form a 4-morpholinyl, pyrrolidinyl or piperidinyl ring;

R^{20} and R^{27} are each independently H; C_1-C_4 alkyl; C_1-C_4 haloalkyl; C_2-C_5 alkylcarbonyl; phenylcarbonyl optionally substituted with R^{21}; C_3-C_4 alkenyl; C_3-C_4 alkynyl; phenylmethyl optionally substituted with R^{21} on the phenyl ring; C_1-C_4 alkylsulfinyl; C_1-C_4 alkylsulfonyl; phenylsulfinyl, phenylsulfonyl or phenoxycarbonyl each optionally substituted with R^{21}; C_2-C_4 alkoxycarbonyl; $C(=O)NR^{22}R^{23}$; $C(=S)NHR^{23}$; $P(=S)(C_1$-C_4 alkoxy$)_2$; $P(=O)(C_1$-C_4 alkoxy$)_2$; or $S(=O)_2NR^{22}R^{23}$;

R^{22} is H or C_1-C_3 alkyl;

R^{23} is C_1-C_4 alkyl; or phenyl optionally substituted with R^{24}; or

R^{22} and R^{23} can be taken together along with the nitrogen atom to which they are attached to form a 4-morpholinyl, pyrrolidinyl, piperidinyl or imidazolyl ring;

R^{25} is 1-2 halogen; C_1-C_4 alkyl; C_1-C_4 haloalkyl; C_1-C_4 alkoxy; C_1-C_4 haloalkoxy; nitro; cyano or C_1-C_4 alkylthio; and

R^{28} is halogen; cyano; nitro; hydroxy; hydroxycarbonyl; C_1-C_6 alkyl; C_3-C_6 cycloalkyl; C_1-C_6 haloalkyl; C_1-C_4 alkylthio; C_1-C_4 alkylsulfinyl; C_1-C_4 alkylsulfonyl; $(C_1$-C_4 alkyl$)_3$silyl; C_2-C_5 alkylcarbonyl; C_2-C_4 alkenyl; C_3-C_4 alkenyloxy; C_2-C_4 alkynyl; C_3-C_4 alkynyloxy; C_1-C_4 alkoxy; C_1-C_4 haloalkoxy; C_2-C_4 alkoxyalkyl; C_2-C_5 alkoxycarbonyl; C_2-C_4 alkoxyalkoxy; $NR^{15}R^{16}$; $C(=O)NR^{17}R^{18}$; or phenyl, phenoxy or phenylthio each optionally substituted with R^{26};

provided that

when E is, C_1-C_6 alkylthio, C_1-C_6 alkoxy, C_1-C_6 haloalkoxy, phenoxy, phenylthio or phenylamino, then E may only substitute compounds of Formula I;

and agriculturally suitable salts and metal complexes thereof and at least one of (a) a surfactant, (b) an organic solvent and (c) at least one solid or liquid diluent.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/03583

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C07D413/04; C07D417/04; A01N43/88

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C07D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
P,A	WO,A,9 211 249 (DU PONT DE NEMOURS) 9 July 1992 * claims *	1-10
A	CHEMICAL ABSTRACTS, vol. 83, 1975, Columbus, Ohio, US; abstract no. 10171, POTEKHIN, A. A., NIKOLAEVA, N. M. '5,6-Dihydro-4H-1,3,4-oxadiazines.' see abstract & SU,A,461 929 28 February 1975 cited in the application	1-10

-/--

° Special categories of cited documents:[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
13 JULY 1993	26. 07. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Bernd Kissler

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	CHEMICAL ABSTRACTS, vol. 90, 1979, Columbus, Ohio, US; abstract no. 152131, DOVLATYAN V V; GEVORKYAN R A 'Synthesis of pesticides. Reactions of halonitriles with esters of s-triazinyldithiocarbazic acid.' see abstract & ARM. KHIM. ZH. (AYKZAN,05159628); 78; VOL.31 (11); PP.851-6	1-10
A	CHEMICAL ABSTRACTS, vol. 87, 1977, Columbus, Ohio, US; abstract no. 102359, DOVLATYAN V V; GEVORKYAN R A 'Synthesis of pesticides. II. Study of the reaction of potassium hydrazino-s-triazine with chloroacetonitrile and .alpha.,.beta.-dichloropropionitrile and its urotropine salt' see abstract & ARM. KHIM. ZH. (AYKZAN,05159628); 77; VOL.30 (10); PP.851-4	1-10
A	CHEMICAL ABSTRACTS, vol. 89, 1978, Columbus, Ohio, US; abstract no. 43349, DOVLATYAN V V; GEVORKYAN R A 'Oxadiazinyl-s-triazine derivatives' see abstract & SU,A,556 143 (ARMENIAN AGRICULTURAL INSTITUTE; USSR) 30 April 1977	1-10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/03583

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/

The definition of the following substituent(s) is too general and/or encompasses too broad a range of totally different chemical groups, only partly supported by examples given in the descriptive part of the application:

X, Y, G1, G2, G3, E

The number of theoretically conceivable compounds resulting from the combination of all claimed substituents of above list precludes a comprehensive search. Guided by the spirit of the application and the inventive concept as disclosed in the descriptive part of the present application the search has been limited to the following case(s):

1. 4-(2-Pyridyl or 2-Pyrimidyl or 2-Triazinyl)-1,3,4-Oxa/thiadiazines
2. 4-(2-Pyridyl or 2-Pyrimidyl or 2-Triazinyl)-1,3,4-Oxa/thiadiazepines
3. 4-(2-Pyridyl or 2-Pyrimidyl or 2-Triazinyl)-1,3,4-Oxa/thiadiazocines

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9303583 SA 73324

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 13/07/93
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9211249	09-07-92	AU-A- 9127091	22-07-92
		CN-A- 1062726	15-07-92